PAPER CHROMATOGRAPHY OF METAL IONS WITH SPECIAL REFERENCE TO ANTIMONY TIN AND MERCURY

THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

THE ALIGARH MUSLIM UNIVERSITY
ALIGARH

MUKHTAR AHMAD KHAN

October 1965

of the different valence states of a metal ion and the latter needs specialized equipment. Interference in these separations from other cations has also been studied.

Precipitation chromatography of silver and mercury has been studied on strontium chromate papers to achieve fast and semiquantitative determinations. It has been found possible to determine approximately five micrograms of Ag(i) and Hg(i) in the presence of many common cations.

Since paper chromatography is being used more and more for the separation and determination of metal ions it is important to have some criterion by which one could predict a suitable solvent system. Attempts have been made to study the use of dielectric constant for this purpose. Hence a detailed study has been made of the effect of dielectric constant on the Rf values of metal ions in various alcohol-formic acid systems. It has been shown that it is generally possible to explain Rf values of most metal ions in alcohol-formic acid system on the basis of D.E.C. As, Sb and Sn have been found to show an exceptional behaviour.

The distribution of Sb^{125} as $SbCl_3$ has been studied between anisole and aqueous formic acid and it has been found that 3M is the optimum HCl concentration for extraction of $SbCl_3$ in the organic phase.

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(1) Summary i - P 2.

C O N T E N T S

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A C K N O W L E D G M E N T

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A B S T R A C T

Paper chromatography of metal ions has been studied with special reference to tin antimony and mercury. Successful methods have been developed for the separation of tin and antimony which were rather difficult to separate by paper chromatography. Fast and selective separations of the different valence states of Sb and Hg by paper chromatography are described. Semiquantitative determinations of Ag and Hg have been achieved by precipitation chromatography.

The chromatography of numerous metal ions have beeh studied in different alcohol-formic acid systems and correlation has been developed between the dielectric constant of the solvent system and the Rf values of the cations. Finally the distribution coefficient of $SbCl_3$ has been measured in anisole-aqueous formic acid systems using radioactive methods.

List of Publications

(i). Paper chromatography of Sn^{+2} and Sb^{+3}.
J.Chromatog. 8, 276 (1962).

(ii). Fast paper chromatography of Hg and Sb.
Anal.Chem., 35, 2050 (1963).

(iii). Paper chromatography of cations in alcohol-formic acid system.
J.Indian Chem.Soc., 41, 673 (1964).

(iv). Effect of dielectric constant on Rf values of cations.
Talanta, ... (In press).

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List of Figures

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CHAPTER I

I N T R O D U C T I O N

Of the various analytical techniques available for the separation and determination of metal ions, paper chromatography is especially suitable for handling micro-amounts of complex mixtures (14,26). It is possible in this way to get rid of many interferences rapidly and efficiently. The method is so versatile that by proper selection of solvent system (18,24,27,32), temperature (3,17,35,43), and impregnating agents (8,9,10,12,34,40), it is possible to resolve any mixture into its components.

In fact the variations possible in the technique of paper chromatography are determined only by the limit of human ingenuity. A particularly important example is the separation of platinum metals using $SnCl_2$ - HCl systems as solvent. The metals form Sn^{+2} complexes in situ and are then easily separated from one another (30). For this reason chromatography has found applications not only in industry (36,49) but also in theoretical studies (13,29,47, 54). A novel application is the analysis of a two component mixture of ions e.g. La-Y by means of chromatographic spectra (33).

The separations achieved by paper chromatography depend primarily upon the distribution of the solute between stationary and mobile phases (17,21,39,55). Other factors like ion exchange (1,28,44,45) and adsorption (15, 32,42,50) are also responsible to a certain extent in effecting the differential migration of ionic species on paper. For instance it was shown by Ackermann (1) that the ion exchange capacity of a paper is proportional to its cellulose content which is reduced by acid washing but restored by alkali treatment.

The distribution of solute between two phases is governed by numerous physical interactions which are exhibited by the solute for the stationary and mobile phases (19). It is therefore clear that the solvent composition (2,4,5,6,7,16,20,22,23,24,25,29,31,37,38,41,46,47,48,49,51, 52,53,54) has a very important role to play in the chromatography of ionic and non ionic species. For these reasons in the last few years there has been renewed interest in the fundamental aspects of paper chromatography (37,38,46, 47). Thus A.J. Tomisek (53) found that control of water content of paper is necessary for reproducible results in chromatography. It is the desire of every analytical chemist to be able to predict the solvent system applicable

to the particular problem (11,21). With these ideas in mind equations have been developed which can correlate the Rf values of a substance in a complex solvent system if the Rf values of the same substance are known in pure components composing the complex solvent system (51). The present work was therefore undertaken with two objectives in mind: (i) To develop better and more useful methods for some difficult and important separations and in this way to extend the utility and application of this technique in inorganic analysis. (ii) To correlate as far as possible the Rf values of metal ions in untreated papers with solvent composition. To study the first aspect we decided to concentrate on common metals like tin, antimony, and mercury. Some of the problems which we have tackled are: (i) Separation of Sn^{+2} and Sb^{+3} which was rather difficult to achieve paper chromatographically.
(ii) Separation of different valence states of antimony and mercury for which fast and selective solvent systems were not available. (iii) The separation of mercurous and silver from numerous metal ions by precipitation chromatography.

To study the second aspect, we decided to investigate the migration of numerous metal ions in alcohol - formic acid systems. Thus keeping formic acid common in all these systems it was possible to explore the effects on the migration of ions due to small changes in composition of the solvent system which resulted when one member of the homologous series of alcohols was substituted by another. By such a systematic study we could also interpret the effect of dielectric constant on the Rf values of metal ions. Since polarity of a system is hard to define it is useful to have some easily measurable property which can help in the proper selection of solvent systems. We have tried to find out the value of dielectric constant for solving this particular problem.

We also tried to study the distribution of Sb^{+3} between formic acid and anisole. Since this solvent system was very helpful in separating Sn^{+2} and Sb^{+3} it is quite likely that it may find some utility in the separation of the two substances by solvent extraction. Using Sb^{125} we studied the distribution of antimony trichloride between anisole and aqueous formic acid. More work on similar lines is necessary for Sn^{+2} before it will be possible to correlate the Rf values of these ions with

their distribution coefficients and to ascertain the utility of anisole - formic acid system for the separation of Sn(ii) and Sb(iii).

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CHAPTER II

Separation of Sn^{+2} and Sb^{+3}

Arsenic, antimony, and tin form 2nd B group in the separation scheme of Fresinius. However arsenic is easy to separate from tin and antimony. Sn^{+2} and Sb^{+3} are rather difficult to separate owing to the fact that their properties resemble very closely. They occupy similar positions in the periodic table. Thus tin is in IV B group and antimony finds place in V B group. Their electronic structures are given below:

Sn (50) $1s^2$, $2S^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$ $5s^2$, $5p^2$.

Sb (51) $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $5s^2$, $5p^3$.

In the formation of Sn^{+2} the last two p electrons are removed while in the formation of Sb^{+3} the last three p electrons are lost. Sn^{+2} and Sb^{+3} have therefore the same electronic structures except for the difference in the

number of positive charges. This probably explains their similar properties and accounts for the difficulties experienced in their separation.

Paper chromatography also does not offer a very neat and successful method for this separation (3). Pollard (4) separated the two ions using collidine saturated with dilute nitric acid in 35 hours. Burstall's separation of the two cations with acetyl acetone-dilute hydrochloric acid (saturated) was not satisfactory since Sn^{+2} tailed from the solvent front (1). Oxidation of cations to their higher valence states prior to chromatography, a method advocated by Harasawa, also failed (2). The method proposed by Stefanovic (5) required twenty one hours and could not be reproduced by us. The present study was therefore undertaken to develop a suitable and selective separation of the two cations.

E X P E R I M E N T A L

Test solutions: Cation solutions were 0.1 M except tin (ii) and antimony (iii) chlorides, which were 0.2 M. Nitrates of Ag^{+}, Pb^{+2}, Cu^{+2}, Cd^{+2}, Al^{+3}, Cr^{+3}, Co^{+2}, Mn^{+2} Ni^{+2}, Zn^{+2}, Ca^{+2}, Ba^{+2}, Sr^{+2}, Mg^{+2}, Be^{+2}, Th^{+4}, Tl^{+}, UO_2^{+2}, Ce^{+3}, Zr^{+4} and La^{+3} were dissolved in distilled water with sufficient nitric acid to prevent hydrolysis. Arsenous oxide, bismuth chloride, and ferric chloride were dissolved in 4M hydrochloric acid. 1.89 gms stannous chloride and 2.0 gms antimony trichloride were dissolved in 15 ml hydrochloric acid and diluted to 50 ml by distilled water. 5% sulphuric acid was used to dissolve vanadyl sulphate and ferrous sulphate.

Reagents: All reagents used were in the purest form available. Acids formic, acetic, propionic, butyric, isovaleric, oxalic and citric; propanol, isopropanol, pentanol, octanol, allyl alcohol and cyclohexanol; acetyl chloride, ethyl acetate, propyl acetate; acetone, ethyl methyl ketone, cyclohexanone and acetyl acetone were E.Merck products. B.D.H. reagents used were: Lactic acid, tartaric acid, benzoic acid, methanol, butanol, isobutanol, palmitoyl chloride, acetic anhydride,

acetaldehyde, formaldehyde, 2:4-hexandione, aniline, quinoline, ammonium oxalate, ammonium carbonate, ammonium chloride, glucose, naphthalene, sodium chloride and potassium chloride. Anisole from W.J.Bush (London) was used. Ethanol was purified by double distillation. Spot solutions were made from B.D.H. or E. Merck products.

Apparatus and Procedure: Ascending chromatography was performed in 15 x 5 and 30 x 5 cms museum jars. Shandon glass cabinet was used for descending work. S & S 3043a and Whatman No.1 papers stripped into convenient sizes were taken. 11.5 cms Whatman No.1 circles were used for Kawerau circular chromatography apparatus.

Thin glass capillaries were used for spotting and one spot (approx.0.002 ml) of the test solution was applied. The paper was conditioned for fifteen minutes in ascending and thirty minutes in descending chromatography. Time of development was forty five minutes, two hours, and twenty minutes for ascending, descending, and circular chromatography respectively.

Detection: Detection was performed with standard chromatographic reagents. Yellow ammonium sulphide was used for Ag^{+}, Hg_2^{+2}, Hg^{+2}, Pb^{+2}, Cu^{+2}, Cd^{+2}, Bi^{+3}, As^{+3}, Co^{+2}, Ni^{+2} and Tl^{+}. Al^{+3}, Cr^{+3}, Zn^{+2}, Mn^{+2}, Ca^{+2}, Mg^{+2} and Be^{+2} were located by 0.5% alcoholic solution of aluminon, made alkaline with ammonia. Alizarine (0.1% in alcohol) detected La^{+3}, Ce^{+3}, Zr^{+4}, V^{+4} and Th^{+4}. 0.5% Alcoholic rhodizonic acid was used for Ba^{+2} and Sr^{+2}. UO_2^{+2} and Fe^{+3} were detected with potassium ferrocyanide and phosphomolybdic acid (10% aqueous) was used for Sn^{+2} and Sb^{+3}.

R E S U L T S

(a) Separation of stannous and antimonous ions.

A large number of pure organic liquids and inorganic solutions were tried for this separation. Some of the developers were:

Propionic acid, butyric acid, isovaleric acid, palmitoyl chloride, acetyl chloride, acetic anhydride, aniline, diethyl amine, methyl cyclohexanone, anisole, ethanol, methanol, n propanol, n butanol, n pentanol, isobutyl alcohol, isopropyl alcohol, acetaldehyde, propionaldehyde,

formaldehyde, quinoline, 2:4-hexandione, lactic acid, 10% solutions of urea, thiourea, succinic acid, tartaric acid, citric acid, ammonium chloride, sodium chloride, potassium chloride and sodium bisulphite. Rf values of the two cations in some of the pure solvents are given in Table I.

T A B L E - I

Rf values of Sn^{+2} and Sb^{+3} in some pure solvents.

Solvent	Sn^{+2} Rf	Sb^{+3}
Water	0.5 T	0.00 T
Methanol	0.75	0.00 & 0.68
Ethanol	0.73 T	0.00 T
n Propanol	0.70 T	0.52 E
n Butanol	0.00 & 0.62	0.00 T
Isobutanol	0.70	0.53 T
n Pentanol	0.62 T	0.00 T
Glycol	0.70	0.82
Acetone	0.86	0.00 & 0.3 T
Formic acid	0.32	0.41

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Acetic acid	0.17 E	0.44 E
Acetic anhydride	0.64	0.6 T
Propionic acid	0.10 E	0.30
Butyric acid	0.00 T	0.00 and 0.20
Isovaleric acid	0.06	0.00 and 0.15
Ethyl acetate	0.00 T	0.00 and 0.21
Ethyl propionate	0.16 E	0.36 E
Ethyl benzoate	0.00	0.16 E
Aniline	0.19	0.00
10% Urea	0.7 T	0.00 T

T : Tails; E: Elongated

The chromagraphic paper was impregnated with ammonium carbonate, glucose, naphthalene, ammonium oxalate, benzoic acid and sodium thiosulphate etc., prior to the development. Double development of the paper showed good results which are summarized in Table II.

T A B L E - II

R_f values of Sn^{+2} and Sb^{+3} with double development of the chromatogram.

First Developer	Second Developer	Sn^{+2} R_f	Sb^{+3}
Formic acid	n Propanol	0.72	0.52
Glycol	Acetic acid	0.71	0.80
Iso-butanol	Urea 10%	0.72	0.55
Formic acid	Urea 10%	0.60	0.51

A reference to Table I shows that formic acid is the only solvent which causes differential migration of the two ions on paper and gives reasonably compact spots. Further studies were therefore made to explore the utility of this solvent. The results are summarized in Table III.

T A B L E - III

Separation of Sn^{+2} and Sb^{+3} by ascending chromatography in solvents containing formic acid.

Solvent	Sn^{+2}	R_f	Sb^{+3}	Time in hours
Formic acid-Anisole (1:1)	0.26		0.54	2
Formic acid-Anisole (1:2)	0.14		0.44	2
Acetic acid-Formic acid (1:1)	0.33		0.47	2
Acetic acid-Formic acid (1:2)	0.42		0.53	2
Formic acid-Butyric acid (1:1)	0.36		0.52	2
Formic acid-Propionic acid (1:1)	0.19		0.41	2
Formic acid-Propionic acid (1:2)	0.16		0.40	2

Similar separations were also obtained using the descending and circular methods. The results are given in Tables IV and V.

T A B L E - IV

Separation of Sn^{+2} and Sb^{+3} by descending chromatography.

Solvent	Sn^{+2}	R_f	Sb^{+3}	Time in hours.
Formic acid-Anisole (1:1)	0.14		0.50	2
Acetic acid-Formic acid (1:2)	0.39		0.47	2
Formic acid-Butyric acid (1:1)	0.31		0.46	2
Formic acid-Propionic acid (1:1)	0.33		0.48	2

T A B L E - V

Circular paper chromatography of Sn^{+2} and Sb^{+3}.

Solvent	Sn^{+2}	R_f	Sb^{+3}	Time in minutes.
Formic acid-Anisole (1:1)	0.39		0.67	20
Acetic acid-Formic acid (1:2)	0.51		0.67	20
Formic acid-Butyric acid (1:1)	0.33		0.53	20
Formic acid-Propionic acid (1:1)	0.36		0.62	20

Best results with all the three techniques were obtained with formic acid-anisole (1:1).

Selectivity of the separation in this system was tested for a large number of eations. Solutions of tin (ii) antimony (iii), and impurities were spotted on the paper in the ratio (1:1:1). The results are recorded in Table VI.

T A B L E - VI

Separation of Sn^{+2} and Sb^{+3} in presence of impurities.

Impurity added	Sn^{+2} R_f	Sb^{+3} R_f	Distance in cms between two spots
Ag^{+}	0.25	0.60	1.4
Hg^{+2}	0.23	0.56	1.4
Hg_2^{+2}	0.27	0.60	1.5
Pb^{+2}	0.24	0.57	1.6
Cu^{+2}	0.29	0.58	1.7
Cd^{+2}	0.28	0.58	1.3
Bi^{+3}	0.29	0.58	1.7
As^{+3}	0.36	0.70	1.5
Fe^{+3}	0.27	0.61	1.5
Al^{+3}	0.20	0.61	1.4

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Cr^{+3}	0.30	0.60	1.2
Mn^{+2}	0.24	0.56	1.4
Mg^{+2}	0.23	0.60	1.5
Zn^{+2}	0.34	0.58	1.1
Ni^{+2}	0.24	0.60	1.5
Co^{+2}	0.20	0.52	1.2
Ca^{+2}	0.24	0.58	1.3
Ba^{+2}	0.23	0.61	1.6
Sr^{+2}	0.26	0.56	1.7
Sn^{+4}	0.26	0.60	1.4

(b) Detailed study of the formic acid-anisole system.

To study this solvent system in detail a number of factors were varied. The more important among them were time of development, time of conditioning, and period of storage. Results are shown in the Tables VII, VIII and IX.

T A B L E - VII

Effect of time of development on Sn^{+2} and Sb^{+3} separation.

Time of development in minutes.	R_f Sn^{+2}	Sb^{+3}	Distance between two spots in Cms.
8	0.21	0.56	0.20
10	0.27	0.58	0.30
15	0.19	0.42	0.40
20	0.21	0.50	0.80
30	0.21	0.58	1.3

It is evident that satisfactory separation is possible in 8 minutes. However a better separation is obtained in approximately half an hour.

T A B L E - VIII

Effect of period of conditioning on Sn^{+2} and Sb^{+3} Separation.

Time of conditioning in minutes.	R_f Sn^{+2}	Sb^{+3}	Distance between the two spots in cms.
0	0.28	0.50	0.20
10	0.25	0.58	0.30
20	0.26	0.60	0.30
30	0.27	0.50	0.40
40	0.24	0.52	0.40
50	0.28	0.60	0.40

Earlier studies had shown that if the solvent is left open it deteriorates quickly probably by absorbing moisture from the atmosphere. Change in efficiency of the solvent on storing was therefore studied by preparing anisole-formic acid (1:1) mixture and storing it in a tightly corked bottle. Rf values were determined at regular intervals. Results are summarized in Table IX.

T A B L E - IX

Effect of storage of anisole-formic acid solvent on Sn^{+2} - Sb^{+3} separations.

Period of storage of solvent in hrs.	R_f Sn^{+2}	Sb^{+3}	Distance between the two spots in cms.
0	0.20	0.53	1.4
6	0.23	0.62	1.3
12	0.32	0.61	0.8
18	0.26	0.52	0.8
24	0.32	0.51	0.7
36	0.25	0.45	0.40

The results show that on standing the efficiency of separation is decreased. However the solvent keeps in fairly good condition for about six hours.

Since anisole-formic acid is a new solvent on which no chromatographic work has been reported, it was decided to investigate the Rf values of important cations in this solvent system. Results are given in Table X.

T A B L E - X

Rf values of common cations in anisole-formic acid (1:1).

Cation	R_f	Cation	R_f
Ag^{+}	0.00	Al^{+3}	0.35
Hg_2^{+2}	0.00	Ce^{+3}	0.00, 0.28
Hg^{+2}	0.00, 0.50	Zn^{+2}	0.31
Pb^{+2}	0.05	Mn^{+2}	0.32
Cu^{+2}	0.28	Ni^{+2}	0.26
Cd^{+2}	0.12 E	Co^{+2}	0.26
Bi^{+3}	0.24	Ca^{+2}	0.40
As^{+3}	0.05 E	Ba^{+2}	0.00 & 0.32
Sn^{+2}	0.26	Sr^{+2}	0.44

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Sb^{+3}	0.58	Mg^{+2}	0.35
Fe^{+2}	0.22	Uo_2^{+2}	0.33
Fe^{+3}	0.30	Th^{+4}	0.2 E
Be^{+2}	0.43	La^{+3}	0.29
Zr^{+4}	0.07 E	Ce^{+3}	0.24
V^{+4}	0.30 E	Tl^{+}	0.43
Ti^{+3}	0.00 T	-	-

To extend the utility of this solvent system for inorganic separations some synthetic mixtures were spotted and separated on paper. The results are shown in Table XI.

TABLE - XI

Separation of

Synthetic mixtures with anisole-formic acid (1:1)

Mixture	Rf	Distance between the spots in cms.
Cu^{+2}	0.22	-
Ag^{+}	0.00	0.80
Pb^{+2} or Ag^{+} or Hg_2^{+2}	0.00	
Sn^{+2}	0.26	1.0
Sb^{+3}	0.54	1.4

Tl^{+} from	0.40	0.6
Pb^{+2}	0.05	Pb^{+2}, Hg^{+2}_{2}, Cd^{+2}
Hg^{+2}_{2}	0.00	and As^{+3} give
Cd^{+2}	0.12	almost mixed spots.
As^{+3}	0.05	

D I S C U S S I O N

It is clear from above that anisole-formic acid offers a simple and reproducible solvent system for the separation of Sn^{+2} and Sb^{+3}. Formic acid is useful in this separation because besides providing an acidic medium it also acts as a reducing agent and therefore it prevents the oxidation of the cations to their higher valence states. The separation of two ions is not effected by the presence of common impurities (Table VI). The relation between the time of development and distance between the spots is not linear. The increase in the distance is greater for larger intervals of time. The effect of conditioning on the distance between the outer boundaries is shown in Table VIII.

It is clear from the perusal of this table that after half an hour an increase in the time of conditioning does not effect the separation. Some of the useful separations in this system are shown in Table XI. Most metal ions do not show high R_f values because the system is only moderately polar.

R E F E R E N C E S

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C H A P T E R - III

Paper Chromatography of different valence states of Mercury & Antimony.

Separation of different valence states of metal ions is important in kinetic studies and in elucidating the mechanisms of reactions (13). It is also useful in the analysis of soils, minerals and rocks. In the analytical laboratory oxidation-reduction systems are often used, and to test the success of a particular operation one should be able to separate and detect the various species involved in the system. Paper chromatography offers a very simple method for these separations. The use of chromatographic methods for these separations allows unfavourable ratios of the two species in micro-amounts to be more easily separated than by standard methods of qualitative analysis (8).

The time of separation is a particularly important factor in the paper chromatographic separation of a metal in different valence states. If the separation time is long enough some interconversion of valence state may occur. Also, one of the valence states Sb^{+5} in the present case-may be sufficiently reactive to interact slowly with the paper or the solvent system. Several

Techniques may be utilized to decrease the separation time including the use of higher temperature, centrifugal chromatography or choice of a proper solvent system. A higher temperature may increase the rate of interconversion as well as decrease the separation time and centrifugal chromatography requires specialized equipment. Therefore the choice of a proper solvent system offers the simplest solution to the problem.

The importance of study of such separations has been discussed (1,9,13). However a survey of literature showed that very few systematic studies have been made of the separation of different valence states by paper chromatography. The more important separations are summarized in Table XII.

T A B L E - XII

Some important separations of different valence states of elements.

Cation	Solvent	Reference
As^{+3} - As^{+5}	Ethyl ether-Methanol-Aq.Hydrochloric acid	Pollard[9]
Ce^{+3} - Ce^{+4}	Butanol-Aq.Hydrochloric acid	Lederer[2,6]
Co^{+2} - Co^{+3}	-	Stevens[13]
"	Ethyl ether-Methanol-Aq.Hydrochloric acid	Pollard[9]
Cr^{+3} - Cr^{+4}	"	"
Cr^{+2} - Cr^{+3} Cr^{+6}	Butanol-Methanol-Acetic acid-Water	Bighi[1]
Cu^{+} - Cu^{+2}	Ethyl ether-Methanol-Aq.Hydrochloric acid	Pollard[9]
"	Pyridine - Water	Bighi[1]
"	Ethanol-Acetic acid-Acetic anhydride	Stevens[13]
Fe^{+2} - Fe^{+3}	Butanol-Acetyl acetone Nitric acid-water	Szarvas[16]
"	Butanol-15% Hydrochloric acid	Bighi[1]
"	Butanol-Ethanol-Acetic acid-Water	Stevens[13]
"	Ethyl ether-Methanol-Aq.Hydrochloric acid	Pollard[10]
"	Butanol-Acetic acid Acetone-Aq. Hydrochloric acid	Qureshi[11]

Fe^{+2} - Fe^{+3}	Butanol-Benzene-Aq.Hydrochloric acid	Kulinska[5]
Hg_2^{+2} - Hg^{+2}	Ethyl ether-Methanol Aq.Hydrochloric acid	Pollard
"	Isopropanol-Nitric acid-Water	Bighi[1]
"	Isopropanol-Hydrochloric acid-water	Carvalho[2,6]
"	Isobutanol-Hydrochloric acid-Nitric acid-Water	Qureshi[12]
"	--	Ivanov[3]
Mn^{+2} - Mn^{+3} Mn^{+3} - Mn^{+4}	Acetic acid-Ethyl acetate	Stevens[13]
Mo^{+3} - Mo^{+5} - Mo^{+6}	Ethyl ether-Thiocyanic acid-water	Stevens[13]
Mo^{+5} - Mo^{+6}	Potassium thiocyanate-Acetic acid-Water	Stevens[14]
"	Ethyl ether-Methanol-Aq. Hydrochloric acid	Pollard[9]
Pt^{+2} - Pt^{+4}	Ethyl ether-Methanol-water	"
Sb^{+3} - Sb^{+5}	"	"
"	Ethyl acetate-Acetic acid-water	Qureshi[12]
Te^{+4} - Te^{+6}	- -	Stienno-Bovy[15]
Ti^{+3} - Ti^{+4}	- -	Kelemen[4]
Tl^{+} - Tl^{+3}	Butanol-Hydrochloric acid-Water	Lederer[2,6]

U^{+4} - U^{+6}	Butanol-Hydrochloric acid-Water	Lederer[2,6]
V^{+4} - V^{+5}	Ethyl ether - Methanol - Acetic acid	Pollard[9]
"	Ethanol - Acetic acid sodium acetate	Stevens[13]

It is apparent from this table that ~~k~~ very little work has been done on fast separations of different valence states of metal ions. From these laboratories a fast separation of Fe^{+2} and Fe^{+3} was reported earlier. We therefore decided to continue these studies for mercury and antimony. These separations have been described by Bighi (1) and Pollard (9). The separation advocated by Bighi could not be reproduced by us. The separation of Sb^{+3} and Sb^{+5} as reported by Pollard requires one hour and Sb^{+5} tails.

Neither Bighi nor Pollard mention the selectivity of these separations. Therefore we decided to make a detailed study of these separations. As a result we have developed faster and more selective solvent system.

E X P E R I M E N T A L

Apparatus, technique, cation solutions used as impurities and the preparation of Sb^{+3} test solution has been described earlier in Chapter II. To obtain M/10 mercury test solutions 3 gms. of freshly prepared mercurous nitrate (E.Merck) were dissolved in 50 ml of 3 M HNO_3 and 2 gms of mercuric nitrate were boiled with

conc. HNO_3 and diluted. 0.2 M $SbCl_3$ solution in hydrochloric acid was boiled with $KClO_3$ cooled and filtered. This was used as Sb^{+5} test solution. 0.2% Acid solution of Rhodamine B was used for the detection of Sb^{+5}. The reagents for Hg_2^{+2}, Hg^{+2} and Sb^{+3} have been reported earlier.

R E S U L T S

(a). Separation of mercurous and mercuric ions.

A large number of pure liquids were tested as developers for this system. Rf values of the two cations in some pure solvents are reported in Table XIII.

T A B L E - XIII

Rf values in various solvents

Solvent	Sb^{+3}	Sb^{+5}	Hg^{+2}	Hg_2^{+2}
Formic acid	0.50	0.40	0.80	0.00 & 0.80
Acetic acid	0.21 - 0.53	0.70	0.50	0.00 T
Propionic acid	0.30	0.48	0.00, 0.60	0.00 T
Butyric acid	0.00 T	0.20	0.00, 0.20	0.00 T
Ethyl acetate	0.00, 0.12	0.00 to S.F.	0.00	0.00 T
Propyl acetate	0.00, 0.20	0.00 to S.F.	0.00	0.00
Methyl alcohol	0.00 T	0.71	0.00 T	0.00 T
Isoamyl alcohol	0.00	0.00, 0.90	0.00 T	0.00 T
Allyl alcohol	0.64	T down from S.F.	0.64 T down	0.00
Dioxane	0.00 T	0.30-0.61	0.00 T	0.00
Isopropyl ether	0.00	0.15	0.00	0.00
Anisole	0.02	0.05	0.00	0.00
Acetone	0.00, 0.2	0.93	0.00 T to S.F.	0.00
Ethylmethyl-ketone	0.00, 0.15	1.00	S.F.	0.00
Acetyl acetone	0.00, 0.20	0.00 to S.F.	0.00	0.00
Isopropyl alcohol	0.72	0.80	0.00	0.00 to S.F.
Water	0.00 T	0.64	0.00, 0.61	0.00 T

The following systems separated Hg_2^{++} from Hg^{++} effectively:

(i) 0.1 M Hydrochloric acid:

The system was simple and gave fast separation (Rf Hg^{+2} = 0.81). Two Rf values remained constant even when the amount of hydrochloric acid was increased from 0.1 to 3 M. In more concentrated acid the spot of Hg^{+2} was elongated.

(ii) 3 M nitric acid - 3 M hydrochloric acid - 15% aqueous ammonium acetate 1:1:6 V/V.

Rf values of both cations remained almost constant (Hg^{+2} = 0.84), when the ratio of Hg_2^{+2}: Hg^{+2} was varied from 1:4 to 4:1. Results were not effected by the increase in concentration of test solutions, i.e. 0.01 M to 0.2 M. The two spots were 1.9 cms apart in 5 minutes. Out of the various cations used as impurities Ag^{+}, Bi^{+3} and Sn^{+2} hindered the separation. Reduction of the Hg_2^{+2} - Hg^{+2} system by Sn^{+2} was quite possible.

(iii) 3 M nitric acid - 3 M hydrochloric acid- Isobutyl alcohol 1:1:10 V/V.

Cd^{+2}, Bi^{+3} and As^{+3} gave significantly different Rf values (0.30, 0.30 and 0.40). from those of Hg_2^{+2} and Hg^{+2} (0.00 and 0.61). Sb^{+3} and Sn^{+2} had

Rf value close to that of Hg^{+2} and the rest of the cations were near Hg_2^{+2} spot.

(iv). 3M nitric acid - 3M hydrochloric acid- Isopropyl alcohol 1:1:10 V/V- The system was most selective. A large number of cations had Rf values different from those of Hg_2^{+2} and Hg^{+2}. Only Cd^{+2}, Bi^{+3}, Sb^{+3}, Ag^{+} and Pb^{+2} interfered. The findings are summarized in Table XIV.

T A B L E - XIV

Rf values of cations in 3M HNO_3-3 M HCl-Isopropanol system (1:1:10 V/V)

Cations	Rf	Cations	Rf
Hg_2^{+2}	0.00	Al^{+3}	0.20
Hg^{+2}	0.66	Cr^{+3}	0.30
As^{+3}	0.43	Mn^{+2}	0.22
Sn^{+2}	0.90	Ca^{+2}	0.20
Fe^{+3}	0.30	Ba^{+2}	0.20
Sr^{+2}	0.24	Bi^{+3}	0.60
Cd^{+2}	0.63	Sb^{+3}	0.61
Ag^{+}	0.00	Pb^{+2}	0.00 T

(b) Separation of Sb^{+3} and Sb^{+5} ions.

Various pure solvents were tested for this separation e.g. Isopropyl ether, chloroform, chloroacetic acid, benzyl cyanide, dioxane, ethyl acetate, ethyl propionate, acetic acid, propionic acid, butyric acid, acetone, pyridine, acetyl acetone, cyclohexanone, acetophenone, ethyl methyl ketone, propanol, isopropanol, butanol, tertiary butanol and anisole. Rf values of the two cations in some of the pure solvents are given in Table XIII.

Good separation was however obtained by glacial acetic acid-water-ethylacetate 1:1:1 V/V. Mixtures of Sb^{+3} and Sb^{+5} in different ratios were successfully separated. Rf values of Sb^{+3} varied from 0.65 to 0.71 and Sb^{+5} was always on the solvent front. Almost all cations were used as impurities to test the selectivity of this separation. The cations whose Rf values differed from Sb^{+3} and Sb^{+5} are given in Table XV. Out of the common cations tried the following showed Rf values close to that of Sb^{+3}.
Hg^{+2} 0.76, Cu^{+2} 0.75, Sn^{+2} 0.78, Al^{+3} 0.64, Cr^{+3} 0.60 and Mn^{+2} 0.60. None of the cations tried had Rf close to that of Sb^{+5}.

T A B L E - XV

Non-interfering cations in Sb^{+3} - Sb^{+5} separations.

Cations	Rf	Cations	Rf
Ag^{+}	0.00 Tails	Co^{+2}	0.47
Pb^{+2}	0.40	Ni^{+2}	0.33
Ca^{+2}	0.58	Zn^{+2}	0.54
As^{+3}	0.50	Sr^{+2}	0.55
Fe^{+3}	0.53	Mg^{+2}	0.50

(c). Double spot formation.

Mercurous ion gave two spots when 15% ammonium acetate and 20% ammonium chloride in water were used as developers. In both cases the Rf values were 0.00 and 0.84. Sb^{+3} gave double spots in a number of cases which are shown in Table XVI.

T A B L E - XVI

Rf values of double spots of Sb^{+3}

Developer	Ist spot	2nd spot
Ethyl acetate	0.00	0.14
Benzyl cyanide	0.00	0.12
5% solution of thiourea in Butanol	0.00	0.50
12 M chloroacetic acid + Isopropyl ether (1:1)	0.00	0.20

D I S C U S S I O N

The separation of Hg_2^{+2} and Hg^{+2} proved more difficult than expected. Acetic acid differentiates fairly well between Hg_2^{+2} and Hg^{+2} (Table XIII). A number of solvent systems containing nitric acid, acetic acid and water in different ratios were tried. In most of these solvents Hg_2^{+2} and Hg^{+2} when applied separately gave different Rf values but when a mixture of two cations was used the separation was not distinct. Best results were obtained with acetic acid - 3M nitric acid - water (3:1:2). If the concentration of nitric acid was less than 3M the mercurous ion was not completely transferred from the point of application, owing to its strong interaction with paper. If on the other hand the concentration of HNO_3 was increased the Hg_2^{+2} was transferred completely from the point of application. The solvent system was then so polar however that the paper did not function as differentiating medium between the two cations. To achieve fast and efficient separations, precipitation chromatography was tried using 0.1 M hydrochloric acid and 15% aqueous ammonium acetate - 3M nitric acid - 3M hydrochloric acid.

The solvents proved to be fast but nonselective. Pb^{+2} and Ag^{+} had Rf values close to zero while all the other common cations had Rf values close to those of Hg^{+2}.

To attain both speed and selectivity complexation chromatography was superimposed on precipitation chromatography. Methyl alcohol was added to the HCl - HNO_3 system. The result was that mercurous ion began to tail owing to its strong interaction with methyl alcohol. When methyl alcohol was replaced by isobutyl alcohol the system became less polar and Hg_2^{+2} gave a compact spot. Three ions gave Rf values significantly different from those of Hg^{+2}. With isopropyl alcohol which is intermediate in polarity between methyl alcohol and isobutyl alcohol, the system became fast selective and efficient.

A reference to Table XIII shows that Sb^{+3} and Sb^{+5} have different Rf values in a number of organic solvents i.e. acetic acid, propionic acid, butyric acid, dioxane, acetone, ethyl methyl ketone, methyl alcohol and isopropyl ether. And, therefore a number of excellent separations are possible with slight modification in these solvents. All efforts to separate Sb^{+3}

and Sb^{+5} using individual organic solvents failed because most of them were not sufficiently polar. Acetic acid gave an elongated spot owing to its low ionization. The addition of water increased the ionization of acetic acid sufficiently to give compact spots. Because of the high polarity of the system however Δ Rf was very small. The addition of ethyl acetate decreased the polarity of the system to such an extent that Δ Rf became significant.

It was noticed in this study that the higher valence state almost always had the higher Rf value. This is easily understood because the higher valence state has a greater covalent character and therefore a greater complexing power. Of the solvents we studied only formic acid appears to be an exception to this trend. The Rf of Sb^{+5} in formic acid is smaller than that of Sb^{+3}.

In the homologous series of fatty acids studied the Rf values decreased with an increase in molecular weight owing to a decrease in the polarity of the system. In this case also formic acid is an exception. The Rf value of Sb^{+5} in formic acid is less than that in acetic acid.

Since chromatography is used more and more as a practical technique importance of time required in a chromatographic separation can hardly be over emphasized. This becomes all the more important if we are considering systems whose composition may change significantly with time such as mixtures of different valence states of the same element.

However time does not occupy the place which it should in our chromatographic data. It is therefore necessary to introduce some new terms in chromatographic literature.

Distance between the two spots may be defined as the distance between the outer boundries of the spots. It is also necessary to define the term effective separation. When distance between the two spots is 1 cm we calb it effective separation. If a mixture contains more than two components then for defining effective separation we consider the components whose Rf values are ~~x~~ nearest to one another. The time of development for effective separation is defined as the time of effective separation or T.E.S. We suggest that T.E.S. is an important characteristic of the separation which must be mentioned together with the Rf value.

It has been observed that some times a separation takes several days and some times it takes only a few minutes. Therefore it is necessary to define a chromatographic separation with respect to time also. The following definitions are proposed.

Name	Time of development
Extra slow paper chromatography	More than 24 hours.
Slow paper chromatography	6 - 24 hours.
Normal paper chromatography	1 - 6 hours.
Rapid paper chromatography	30 mts. - 1 hour.
Fast paper chromatography	0 - 30 mts.

Here time of development refers to the time of effective separation. Time for Hg_2^{+2} - Hg^{+2} separation with HCl - HNO_3 isopropyl alcohol and HCl - HNO_3 - Isobutanol is 10 minutes and the time for Sb^{+3} - Sb^{+5} separation in acetic acid - water - ethyl acetate is 20 minutes. Hence both these separations may be defined as fast.

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C H A P T E R - IV

Effect of Dielectric constant on Rf values of metal ions in some Formic acid - Alcohol systems.

In order to explain and interpret the Rf values of metal ions attempts have been made to correlate them with solvent composition. The effect of concentration and molecular weight of alcohol on Rf values of metal ions in alcohol-water-hydrochloric acid systems was studied by Sommer (23). Hartkamp and Specker (7) interpreted the Rf values in tetrahydrofuran-water-hydrochloric acid systems in terms of transport of different ionic species formed. Carvalho (4,5) studied the effect of water and acid concentration on the chromatographic behavior of metal ions. He traced curves for R_M Vs p H_2O and R_M Vs pcl^- for different butanol-hydrochloric acid-water systems. Soczewinski and Wachtmeister (21,22) have derived a simple relation between R_M values and solvent composition. Martin and Anderson (15) showed from a study of 364 chromatograms that R_p values increase linearly with water and acid concentrations. Effect of acid concentration on R_f values in tributyl phosphate-nitric acid and butanol-hydrochloric acid systems was reported by Kertes (10) and Lederer (13). Some

studies on isopropanol (16,17) and various alcohols with hydrochloric acid (20) have also been recorded. Setty (20) found that R_f values of metal ions (Pt, Pd, Cu except Au), increase with hydrochloric acid concentration in hydrochloric acid-alcohol systems, and decrease with increase in carbon chain of alcohol.

An interesting property of the solvent composition is its D.E.C. (8) which is a measure of the polarity of the solvent system. It is therefore useful to correlate the R_f values of metal ions with the D.E.C. of the solvent system. The effect of dielectric constant on R_f values of metal ions was first investigated by Kertes (9) who found that the R_f values of univalent and bivalent cations increase linearly with D.E.C. of the solvent system. Similar conclusions were arrived at by Ghe and Placucci (6) who studied the cations Mn^{+2}, Co^{+2}, Ni^{+2} and Cu^{+2} in alcohols from methanol to pentanol. In a recent study the R_f values of thiourea, thiocyanate and sulphide have been correlated with the dielectric constant of the solvent (19). These studies suffer from two limitations: (i) The number of solvent systems studied is rather small. (ii) Acid-alcohol systems have been completely neglected even though they are used most in paper chromatography. This reluctance is probably

due to the fact that it may not be easy to interpret the polarity of such binary systems and hence to correlate the R_f values with D.E.C. of the solvent system. A survey of the literature indicated that non-aqueous systems have not been studied extensively (Table XVII). And no systematic study has been reported of the correlation of the chromatographic behavior in metal ions.

It was therefore decided to study the effect of D.E.C. on R_f values of numerous cations in alcohol-formic Acid systems. The R_f values were chosen from a previous formic acid-alcohol study described in Chapter V. The present report summarizes our findings on the correlation of these R_f values with the D.E.C. of the solvent system concerned.

T A B L E - XVII

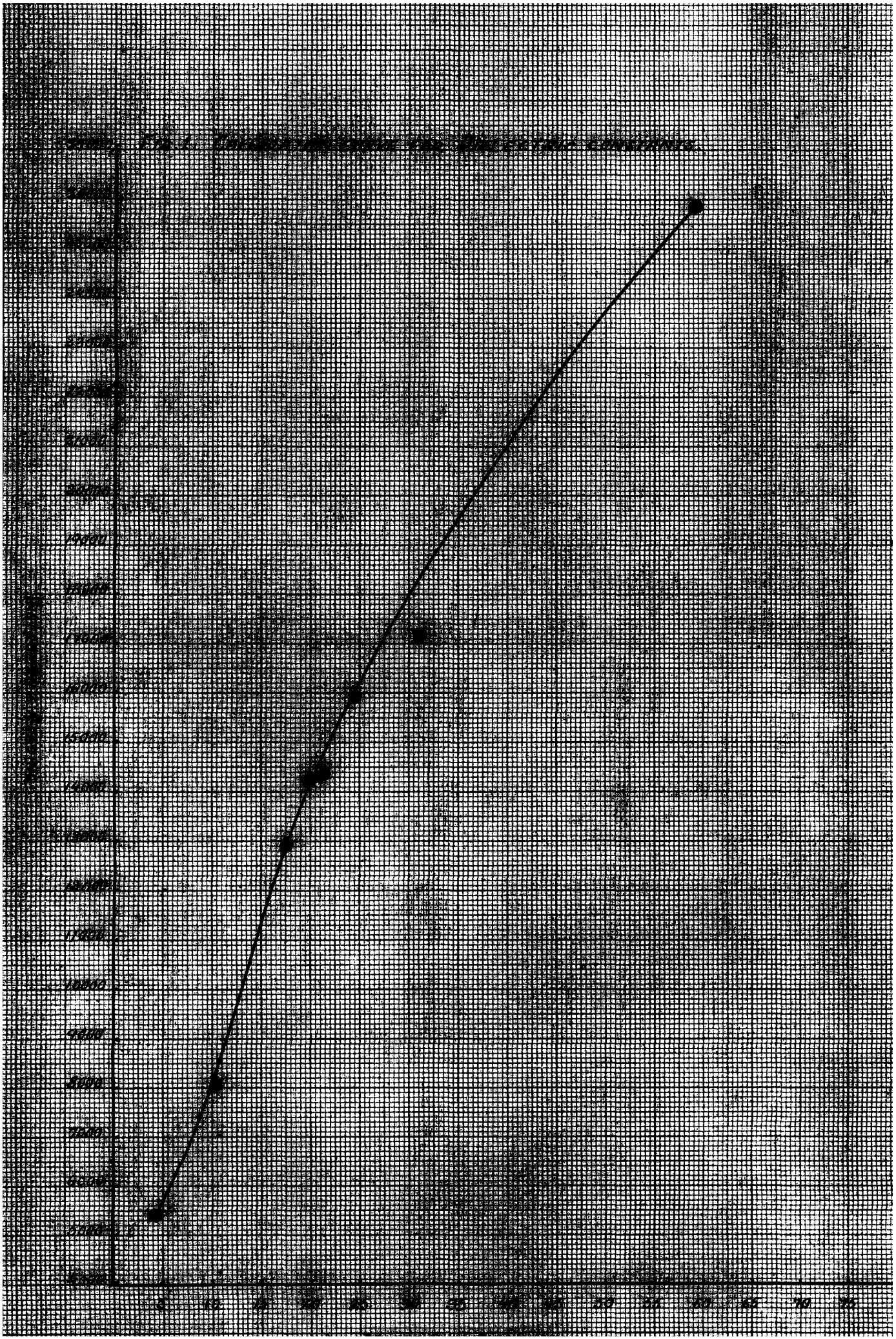
Paper Chromatography of some cations in non-aqueous systems.

System	Cations studied	Reference
Acetic acid-Acetic anhydride.	Mn^{+2}, Mn^{+3}, Mn^{+6}	(24)
Acetone-Methyl acetate (1:1)	La, Ce, Pr, Nd, Sm	(26)
Acetone-Ethyl acetate (1:1)	"	"
Acetone-Propyl acetate (1:1)	"	"
Acetone-Ethyl ether (1:1)	"	"
Benzene-Methanol-Acetic acid (68:30:2)	Mn, Cu, Ni Acetylacetonates	(1)
Butanol-Methanol	Te, Se	(3)
Butanol-Methanol-Ethyl ether (1:1:1)	Au, Pt, Se, Te	(12)
Butanol-Pyridine-Dioxane (7:2:1)	U, Th	(25)
Cyclohexane-Methanol-Dioxane (84:6:10)	Cu, Ni,Co Acetylacetonates	(1)
Ethanol	Fe,Ti,Al,V,Ni,Co	(11)
2-Ethylhexanol-Methanol (3:7)	Li, Na, K	(2)
Iso-amyl alcohol	Fe,Ti,Al,V,Ni,Co	(11)

Isopropanol	Fe,Ti,Al,V,Ni,Co	(11)
Methanol	"	"
Methanol-Dioxane-Pet.Ether	Cu,Fe,Ni,Co Acetylacetonates	(1)
Methanol-Chloroform-Toluene	U, Th	(25)
Methanol-Butanol-Collidine-Acetic acid	Ba,Sr,Ca,Mg,Be	(14)
Methanol-Pyridine-Toluene (7:2:1)	U, Th	(25)
Methanol-Pyridine-Dioxane (7:2:1)	"	"
Methanol-Isopropanol-Formic acid-Ammonium formate	Ba, Ca, Sr, Mg	(18)
Propanol	Fe,Ti,Al,V,Ni,Co	(11)
Pyridine-chloroform-Toluene (7:2:1)	U, Th	(25)

Experimental and Results

The cations were studied in the systems containing formic acid and alcohol in the ratio 1:9, 3:7, 5:5, 7:3 and 9:1 by volume using ascending technique described in previous chapters. The alcohols studied were methanol, ethanol, n-propanol, n-butanol, n-pentanol and n-octanol.



The D.E.C. was determined from a calibration curve (Fig.1) drawn with Sargent Oscillometer Model V. The dielectric constants of the various acid alcohol ratios are summarized in Table XVIII.

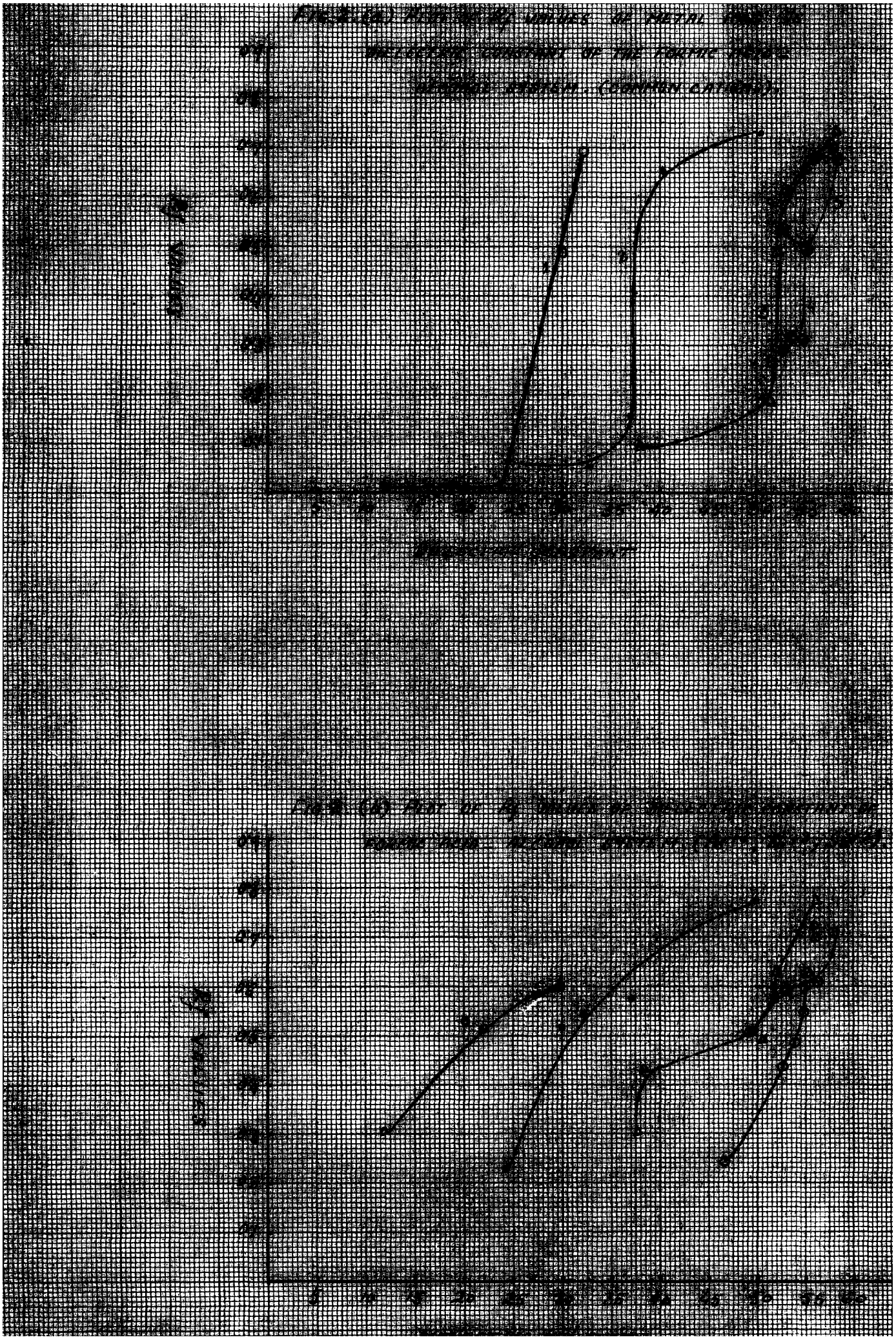
T A B L E - XVIII

D.E.C. of various acid-alcohol ratios.

Acid-alcohol	MeOH	EtOH	PrOH	BuOH	AmOH	Octyl
1:9	30.2	30.0	20.0	18.0	23.5	12.0
3:7	50.0	40.0	37.0	32.0	30	24.8
5:5	56.0	52.0	51.5	51.5	38.2	38.1
7:3	58.0	55.0	55.0	53.5	53.0	47.0
9:1	58.0	56.6	56.0	55.0	53.0	49.0

D I S C U S S I O N

The R_f values of metal ions depend upon a number of factors: (i) formation of metal salts or complexes with acid anion, (ii) solubility and (iii) partition between moving and stationary phases. The last two variables depend upon the polarity of the solvent system.



And since D.E.C. is a measure of polarity it is interesting to correlate the R_f values of metal ions with D.E.C. of the solvent system. It is possible that both R_f values and D.E.C. may depend upon some more fundamental property of the solvent system. However as the following discussion shows a correlation of R_f values with D.E.C. does offer many interesting features. The results obtained from a study of 693 chromatograms have been depicted for the sake of convenience with the help of only three figures. Curve (1) in figure 2 refers to the acid alcohol ratio of 1:9. The D.E.C. is altered by replacing the alcohol present in the system. Formic acid present in the system, is sufficient to prevent tailing but at the same time the acid concentration is not so high as to mask the effect of the alcohol on the migration of the cations. In this system when octanol is replaced by pentanol, butanol or propanol no migration of the cations results since the D.E.C. is not sufficient to cause the migration of the cations. When the D.E.C. is greater than 22 the cations begin to migrate and R_f values increase linearly with D.E.C. The resulting curve may therefore be considered to be made up of two curves (i) $R_f = 0$ and (ii) $R_f = mD + C$. It is interesting to note from figure 2 that once the D.E.C. of the system is greater than 22 there is always

some migration irrespective of the alcohol present or the acid alcohol ratio under consideration.

Curve (2) represents acid alcohol ratio of 3:7. In this ratio R_f is never zero since D.E.C. is always greater than 22. The curve is S shaped. The R_f first increases slowly and then it shows abrupt increase with D.E.C. Finally it levels off because the D.E.C. has become so high that any further increase in D.E.C. has no effect on R_f values. Since 30% formic acid is always present in this solvent system a change in the alcoholic part of the system does not effect the R_f values significantly as it does in the previous ratio. This fact is also noticeable in curves (3) and (4). Finally since curve (5) refers to solvent systems containing a high concentration of formic acid i.e. 90%, it is easily understandable that in these systems any change in the alcoholic constituent should neither alter the D.E.C. significantly nor the R_f values of the cation concerned. All the five curves therefore appear to exhibit a regular trend. To show that this trend is general we have plotted in figure 3 the R_f values of cations Fe^{+3}, Ni^{+2}, Al^{+3} and La^{+3} from curve (i) figure 2. In all cases a plot of R_f Vs D.E.C. gives similar curves. This behaviour therefore appears to be independent of the nature of the cation.

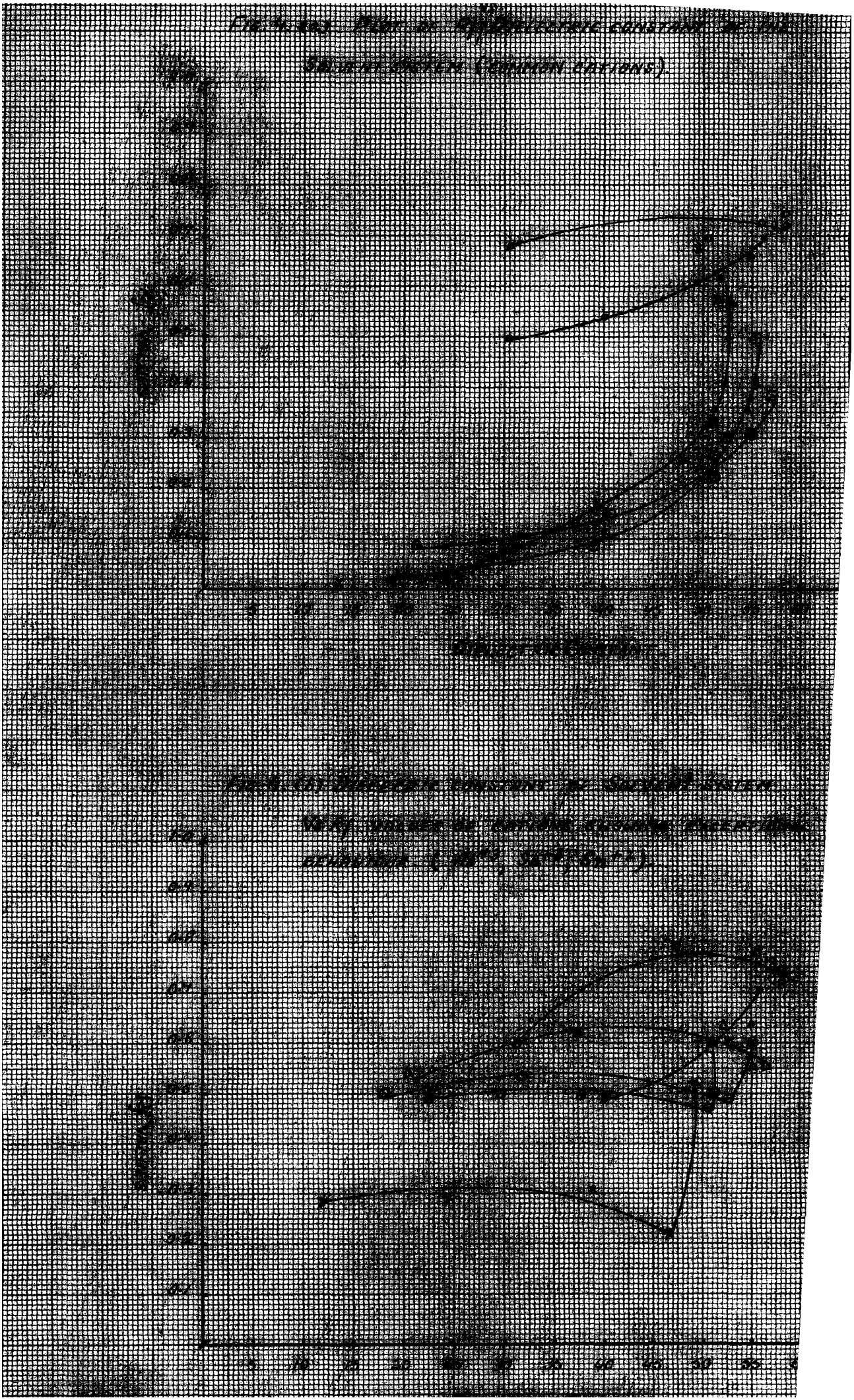


Fig. 2b represents the behavior of As^{+3}, Sb^{+3} and Sn^{+2}. These ions show an exceptional behavior. Even when the D.E.C. is very low they show considerable migration and the lowest R_f is 0.20. However with these cations also R_f value increases with D.E.C. although the increase is linear.

In curve (1) figure 4 we are considering only methanol-formic acid system in which the ratio of components is varied from 1:9 to 9:1. We notice that there is not much change in R_f when we change the D.E.C. of the system by changing the ratio of the components. Methanol itself has a high D.E.C. and addition of formic acid in different ratios does not change the D.E.C. significantly. However with ethanol there is significant change in R_f values as the acid alcohol ratio is changed, since in this case the D.E.C. of the systems is also substantially altered. This trend is even more marked in butanol, pentanol a-nd octanol because they have D.E.C. lower than that of ethanol. The radically different form of curves obtained in figure 4b once again confirms the exceptional behavior of As^{+3}, Sb^{+3} and Sn^{+2}.

From what has been said above it is clear that at low acid concentrations the R_f value increases linearly with D.E.C. for most common cations. This effect of D.E.C. on R_f values can be best studied by using the acid alcohol ratio of 1:9, since the acid concentration in this sytem is sufficient to prevent tailing and at the same time it is not too high to suppress the effect of D.E.C. on R_f values.

R E F E R E N C E S

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C H A P T E R - V

Paper Chromatography of metal ions in Formic acid -Alcohol systems.

Acid alcohol systems are probably the most common in the chromatography of metal ions (20). Most of these systems are summarized in Table XIX. A reference to this table shows that very little work has been done on the use of Formic acid-alcohol systems for the separation of cations. In fact almost no work is available in which the acid alcohol ratio has been continuously varied in the absence of water or any other third substance. Our earlier work on the separation of Sn^{+2} and Sb^{+3} had shown the useful properties of formic acid in cation paper chromatography. Formic acid is an unusual acid in many ways. Even though it is a carboxylic acid yet it has a high ionisation constant (1.77×10^{-4}), and acts at the same time both as an acid and as a reducing agent. It is therefore surprising that so little work has been done on this acid. The present study was therefore undertaken to examine systematically the chromatographic behavior of cations in various formic acid alcohol systems. Such a study proved very beneficial in

developing new separations of tin and antimony from numerous metal ions and in helping the correlation of R_f values with solvent-composition.

T A B L E - XIX

Some acid-alcohol systems used for the paper chromatography of metal ions.

Solvent system	Ions studied	Reference
Hydrochloric acid with	Numerous cations	(1),(2),(6),(10), (12),(25),(26), (30),(35),(36), (48),(50),(57), (59),(60),(63).
(a) Butanol-Water		
(b) Butanol or Ethanol E.D.T.A.-Water	Cd, In	(48)
(c) Butanol-Hydrogen peroxide-water	Ti,V,Mo,Rh,Ir	(24), (30)
(d) Butanol-Butyl chloride-water	Ca,Ba,Sr	(43)
(e) Butanol-Acetone-Acetic acid-water	Fe^{+2}, Fe^{+3}	(56)
(f) Carbitol-Cellosolve-water	Au,Pt,Ru,Pd,Rh	(7)
(g) Cyclohexanol-water	Rare earths	(58)
(h) Ethanol-Water	Various cations	(48),(61)
(i) Ethanol,Propanol, Butanol,Isoamyl alcohol,Benzyl alcohol-water	Numerous cations	(23),(30),31), (39),(67),(68)

(j) Ethanol-Phenol-Water	Al,Ga,In,Tl	(38)
(k) Ethanol-Isopropanol-Ethyl ether-water	Te,Bi	(19)
(l) Isopropanol-water	Numerous cations	(21),(35),(36),(49)
(m) Methanol-Water	"	(25),(45),(47)
(n) Methanol-Butanol-Isobutylmethylketone water	K,Rb,Cs	(43)
(o) Methanol-Ethanol-water	Au,Pt,Ru,Pd,Rh	(7)
(p) Methanol-Phenol-water	Al,Ga,In,Tl.	(38)
(q) Pentanol-Water	In,Tl,Al,Ga	(17)
(r) Pentanol-Benzene-Water	Ti,Al,Fe	(28)
(s) Phenol-water	Various cations	(30)
(t) Propanol-Isobutyl methyl ketone	Rh,Pd,Pt	(24)
Nitric acid with	Numerous cations	(3),(5),(9),(14),(30)
a) Butanol-water		
b) Butanol-Benzoyl acetone,Aceto-acetic ester, Antipyrine-Water	Various cations	(54)
c) Butanol-collidine-Water	Al,Fe,As,Cu,Cd	"
d) Butanol-Propanol-Lithium nitrate-water	Ra,Po,Se,Te & Rare earths	(11)

S U M M A R Y

Paper chromatography of metal ions has been studied not only to develop new methods of analysis but also to study correlation between solvent composition and the R_f values of metal ions. Successful separations have been developed for Sn(ii) and Sb(iii) which were rather difficult to separate by paper chromatography. Anisole-formic acid (1:1), acetic acid-formic acid (1:1), propionic acid-formic acid (2:1) and butyric acid-formic acid (1:1) have been found to give best results.

Fast and selective methods have been developed for the separation of different valence states of Hg and Sb. Time is an important factor in these separations owing to the possibility of interconversion of one valence state into another. Best results for separating Sb^{+3}- Sb^{+5} mixtures have been obtained using acetic acid-water-ethyl acetate (1:1:1). Hg(i) and Hg(ii) are best separated by using the solvent system: isopropanol-3M hydrochloric a 3M nitric acid (10:1:1). In both cases separations are achieved within half an hour. These fast separations h been attained by the proper selection of the solvent system and not either by an increase in temperature (Thermatochromatography) or by centrifugal chromatogra since the former increases the rate of interconversion

e) Butanol-E.D.T.A. Acetylacetone-water	Fe,Ti	(15)
f) Ethanol-Isopropanol water	Various cations	(29)
g) Methanol-Water	"	(8),(42),(47)
h) Methanol,Ethanol, Propanol,Butanol Pentanol,Benzyl alcohol-water	Pt,Pd,Cu,Au	(63)
i) Propanol-Ethyl acetate-Water	Pb	(64)
Hydrobromic acid with Butanol-water	Various cations	(34)
Sulphuric acid with Methanol-water	"	(13),(66)
Thiocyanic acid with Butanol-water	"	(41)
Oxalic acid with		
Methanol-Ethyl acetate-water	As,Sb,Sn,Mo,Pt	(4)
Acetic acid with		
a) Butanol-water	Ag, Hg, Pb	(18)
b) Butanol-oxine-water	Rare earths	(53)
c) Butanol-Acetyl acetone-water	"	(3)
d) Butanol-Aceto acetic ester-water	Cu,Pb,Bi,Co	(32),(54)

e) Butanol-Methanol-Collidine-water	Ba,Ca,Sr,Mg	(37)
f) Ethanol-Water	Various cations	(16),(40),(45)
g) Ethanol-Butanol-water	Fe^{+2}, Fe^{+3}	(65)
h) Ethanol-Isobutanol-water	Pt metals Ag,Au	(22)
i) Methanol-water	Various ions	(50)
Propionic acid with		
Ethanol-Ammonia-water	Alkaline earths	(44)
Butyric acid with		
Isopropanol-Dioxane-Water	Lanthanides, U.,Pr	(46)
Formic acid with		
a) Water	Fe,Al,Ti	(27)
b) Dioxane-Water	"	"
c) Methanol-Isopropanol Ammonium formate-water	Ba,Sr,Ca,Mg	(51)
d) Anisole	Sn, Sb	(55)

E X P E R I M E N T A L

Formic acid (E.Merck) was used. All other reagents were purified by usual means. Whatman No.1 paper was used throughout and the descending technique described in Chapter I was followed. The test solutions and the detection of cations have also been described earlier.

Solvent systems containing the following alcohols were used: Methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl, isoamyl, t-amyl, allyl, octyl, benzyl and cyclohexyl.

R E S U L T S

Rf values of twentynine cations in various formic acid alcohol systems have been recorded in Tables XX - XXXII.

Following abbreviations have been used for the sake of brevity:

M for methanol, E for ethanol, P for n-propanol, IP for isopropanol, B for n-butanol, IB for isobutanol, Am for amyl alcohol, IAm for isoamyl alcohol, T Am for tertiary amyl alcohol, O for octyl alcohol, A for allyl alcohol, Bz for benzyl alcohol and C for cyclohexanol. The alcohol:formic acid ratios studied were (1) 1:9, (2) 3:7, (3) 5:5, (4) 7:3 and (5) 9:1. The ratio numbers are shown in parenthesis. The solvent number consists of a symbol to represent the alcohol used with a subscript to denote the ratio number. Thus M_1 stands for methanol formic acid mixture in the ratio number (i) i.e. 1:9, M_2 signifies methanol formic acid in ratio No.(2) i.e. 3:7 and so on. Rf values of twentynine cations in 65 solvents are thus described. Following curves have been plotted:

Fig.5.

a) Plot of R_f Vs Acid concentration for 24 metal ions in Butanol-Formic acid systems.

b) Plot of R_f Vs Acid concentration for 22 metal ions in Isobutanol-Formic acid systems.

Fig.6.

a) R_f values of most metal ions in Formic acid-Alcohol systems.

b) R_f values of Sn^{+2} and Sb^{+3} in Formic acid-Alcohol systems.

Fig.7. Plot of R_f Vs Acid concentration of some metal ions in Formic acid-Alcohol systems (Cu, Al, Ni, Be, Th, Sn, Sb).

Fig.8. Change in R_f values of most metal ions with increase in C atoms in alcohols.

Fig.9. Separation of Sn^{+2} from numerous cations in cyclohexanol-Formic acid system (7:3).

Fig.10. Separation of Sb^{+3} from numerous cations in cyclohexanol-Formic acid system (7:3).

T A B L E - XX

R_f values of metal ions in Methyl Alcohol-Formic acid systems.

System / Metal ions	M_1	M_2	M_3	M_4	M_5
Ag^{+}					
Hg^{+2}	0.55	0-0.40	0.70 TD	0.66	0-0.64
Hg_2^{+2}	0-0.30	0-0.68	0-0.50	0-0.60	0-0.64
Pb^{++}	0-0.4	0-0.40	0-0.42	0-0.50	0-0.52
Cu^{++}	0.71	0.74	0.75	0.71	0.69
Cd^{++}	0.60	0.58	0.65	0.40	0.67
Bi^{+3}	0.63	0.68	0.62	0.57	0.35
As^{+3}	0.60	0.58	0.53	0.40	0.35
Sn^{+2}	0.72	0.71	0.81	0.83	0.60
Sb^{+3}	0.70 TD	0.70 TD	0.75 TD	0.70 TD	0.50
Al^{+3}	0.80 TD	0.76	0.70	0.72	0.78
Fe^{+3}	0.83	0.80	0.76	0.80	0.72
Cr^{+3}	0.70	0.66	0.55	0.42	0.78
Mn^{+2}	0.71	0.66	0.64	0.52	0.71
Co^{+2}	0.78	-	0.72	0.76	0.84

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Ni^{+2}	0.71	0.73	0.69	0.60	0.75
Zn^{+2}	0.70	0.71	0.68	0.80	0.70
Ca^{+2}	0.64	0.76	0.70	0.70	0.70
Ba^{+2}	0.50 TD	0.50 TD	0.58	0.60	0.80
Sr^{+2}	0.54	0.50	0.55	0.71	0.73
Mg^{+2}	0.70	0.68	0.62	0.60	0.76
Be^{+2}	0.75	0.85	0.88	0.80	0.85
U^{+6}	0.73	0.72	0.78	0.60	0.74
Tl^{+1}	0.24	-	0.33	0.60	-
Th^{+4}	0-0.80	0-0.80	0-0.70	0-0.85	0-0.78
Zr^{+4}	0-0.60	0-0.60	0-0.50	0-0.60	0-0.65
Ce^{+3}	0-0.75	0.75	-	0.81	0.86
V^{+4}	0.71	0.70	0.72	0.68	0.76
La^{+3}	0-0.80	0-0.70	0.72	0.70	0.74

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T A B L E - XXI

Rf values of metal ions in Ethyl alcohol-Formic acid systems.

System Metal ions	E_1	E_2	E_3	E_4	E_5
Ag^{+}	0.00	0.00 T	0.00 T	0.00 T	0.00 T
Hg^{+2}	0-0.70	0.54	0.55	0.60	0.70
Hg_2^{+2}	0.00 T	0.70	0-0.30	0-0.50	0-0.50
Pb^{+2}	0-0.10	0.00	0-0.26	0-0.04	0-0.50
Cu^{++}	0.50 E	0.66	0.50	0.66	0.70
Cd^{++}	0.08	0.30	0.41	0.54	0.62
Bi^{+3}	0.00 T	0.24 E	0.30	0.35 E	0.65
As^{+3}	0.48	0.32 E	0.28	0.20	0.22
Sn^{++}	0.00 T	0.00 T	0.4 E	0.5	0.53
Sb^{+3}	0-0.67	0-0.43	0.5 E	0.60	0.62
Al^{+3}	0 - SF	0.40 E	0.42	0.55	0.73
Fe^{+3}	0 - SF	0.65	0.65	0.70	0.81
Cr^{+3}	0 - SF	0.40	0.45	0.54	0.70
Mn^{++}	0.52	0.40	0.27	0.45	0.70
Co^{++}	0-0.70	0.40 E	0.50	0.60	0.80
Ni^{++}	0.40 E	0.40	0.40	0.60	0.76
Zn^{++}	0.71	0.40	0.50	0.56	0.76
Ca^{++}	0-0.20	0.30	0.55	0.45	0.68

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Ba^{++}	0 - 0.80	0 - 0.20	0.30	0.50	0.68
Sr^{++}	0.20	0.20	0.30	0.40	0.65
Mg^{++}	0.20 T	0.22	0.25	0.50	0.69
Be^{++}	0.65	0.30 E	0.52	0.60	0.74
U^{+6}	0.50 E	0.60	0.45	0.50	0.52
Tl^{+}	0.00 T	-	-	-	-
Th^{+4}	0.00 T	0.00 T	0-0.25	0-0.60	0-0.60
Zr^{+4}	0.00 T	0.00 T	0-0.00T	0-0.30	0-0.50
Ce^{+3}	0.20 E	0.28	0.34 TD	0.60	0.70 TD
V^{+4}	0.00 T	0.00-0.12	0.20	0.35	0.40
La^{+3}	0.30	0.30	0-0.50	0.48	0.60

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T A B L E - XXII

R_f values of metal ions in n-Propyl alcohol formic acid systems.

Metal ions	P_1	P_2	P_3	P_4	P_5
Ag^{+}	0.00 T	0.00 T	0.00 T	0.00 T	0.00 T
Hg^{+2}	0.00 T	0.00 T	0.40	0.55	0.33
Hg_2^{+2}	0.00-.40	0.00 T	0.00-.40	0.58	0.63
Pb^{+2}	0.00	0.04	0.20	0.30TfPA	0.40TfPA
Cu^{+2}	0. .01	0.14	0.28	0.32	0.41
Cd^{+2}	0.00T	0.10	0.34	0.55	0.55
Bi^{+3}	0.00T	0.18	0.32	0.48	0.32
As^{+3}	0.50	0.45	0.44	0.21,0.50	0.40
Sn^{+2}	0.55	0.57	0.64	0.55	0.55C
Sb^{+3}	0.61	0.62	0.53	0.63	0.55C
Al^{+3}	0.00T	0.30	0.35	0.56	0.70
Fe^{+3}	0-SF	0.70	0.00	0.60	0.64C
Cr^{+3}	0.00T	0.15	0.25	0.56	0.65
Mn^{+2}	0.00T	0.20	0.21	0.45	0.60
Co^{+2}	0.00T	0.10	0.30	0.60	0.60
Ni^{+2}	0.00T	0.05	0.21	0.36	0.70
Zn^{+2}	0.00T	0.20	0.30	0.60	0.68

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Ca^{+2}	0.00T	0.15	0.30	0.60	0.65
Ba^{+2}	0.00	0.05	0.20	0.63	0.70
Sr^{+2}	0.00T	0.15	0.34	0.52	0.62
Mg^{+2}	0.00T	0.05	0.23	0.61	0.70
Be^{+2}	0.00T	0.41	0.52	0.71	0.72
U^{+6}	0.00T	0.21	0.20	0.36	0.70
Tl^{+}	0.02	0.05	0-0.30	0.56	0.75
Th^{+4}	0.00T	0.20	0-0.30	0-0.60	0-70
Zr^{+4}	0.00T	0.00T	0.00T	0.12T	0.60T
Ce^{+4}	0.00	0.15	0.24	0.50	0.70
V^{+4}	0.00T	0.08	0.12	0.40	0.66
La^{+3}	0.00T	0.12	0.21	0.61	0.71

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T A B L E - XXIII

Rf values of metal ions in Iso-propyl alcohol-Formic acid systems.

System / Metal ions	IP_1	IP_2	IP_3	IP_4	IP_5
Ag^{+}	0.00T	0.00	0.00	0.00	0.00
Hg^{+2}	0.00T	0.00T	0.40	0.40	0 & 0.50
Hg_2^{+2}	0.00	0.00T	0.30	0.40	0 & 0.40
Pb^{+2}	0.00	0-0.10	0 & 0.30	0.40	0.51
Cu^{+2}	0.00	0.05	0.23	0.33	0.62
Cd^{+2}	0.00	0.10	0.18	0.30	0.55
Bi^{+3}	0.00	0.15	0.20	0.35	0.52
As^{+3}	0.20	0.18	0.20	0.20	0.18
Sn^{+2}	0.51	0.30	0.60	0.55	0.57
Sb^{+3}	0.50	0.20	0.45	0.60	0.62
Al^{+3}	0.70	0.60	0.30	0.60	0.72
Fe^{+3}	0.00T	0.60	0.30	0.60	0.80
Cr^{+3}	0.00T	0.00T	0.20	0.50	0.70
Mn^{+2}	0.08	0.08	0.20	0.55	0.64
Co^{+2}	0.00	0.15	0.30	0.63	0.70

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Ni^{+2}	0.00	0.08	0.26	0.60	0.65
Zn^{+2}	0.00T	0.18	0.25	0.50	0.60
Ca^{+2}	0.20T	0.10	0.20	0.35	0.70
Ba^{+2}	0.00	0.00	0.30	0.52	0.69
Sr^{+2}	0.05	0.10	0.20	0-0.50	0.68
Mg^{+2}	0.00T	0.10	0.20	0.60	0.75
Be^{+2}	0-0.70	0.25	0.40	0.63	0.78
U^{+6}	0.00T	-	0.50	0.56	0.75
Tl^{+}					
Th^{+4}	0.00T	0-0.28	0-0.30	-	0 & 0.70
Zr^{+4}	0.00T	0-0.15	-	0-0.40	0-0.50
Ce^{+4}	0.00T	0.15	0.23	0-0.30	0.75
V^{+4}					
La^{+3}	0.00T	0.18	0-0.30	0-0.30	0.70

T A B L E - XXIV

R_f values of metal ions in n-Butyl alcohol-Formic acid systems.

System / Metal ions	B_1	B_2	B_3	B_4	B_5
Ag^{+}	0.00	0.00	0.00	0.00	0.00
Hg^{+2}	0.00	0.00T	0.41	0.55	0.00T
Hg_2^{+2}	0.00	0.10	0.00 & 0.41	0.00 & 0.60	0.00 & 0.60
Pb^{+2}	0.00	0.00	0.08	0.30	0.51
Cu^{+2}	0.00T	0.05	0.20	0.32	0.50
Cd^{+2}	0.00	0.10	0.22	0.35	0.60
Bi^{+3}	0.00	0.10	0.20	0.30	0.30
As^{+3}	0.08	0.20	0.18	0.15	0.45
Sn^{+2}	0.50	0.55	0.68	0.48	0.62
Sb^{+3}	0.62	0.60T	0.43	0.40	0.50
Fe^{+3}	0.00	0.00T	0.40	0.60	0.75
Al^{+3}	0.00T	0.00T	0.25	0.60	0.68
Cr^{+3}	0.00	0.00	0.31	0.60	0.68
Mn^{+2}	0.00	0.10	0.30	0.40	0.70

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Zn^{+2}	0.00	0.08	0.38	0.50	0.73
Ni^{+2}	0.00	0.05	0.20	0.42	0.72
Co^{+2}	0.00	0.05	0.30	0.50	0.70
Ca^{+2}	0.00	0.05	0.28	0.48	0.72
Ba^{+2}	0.00	0.00	0.28	0.55	0.60
Sr^{+2}	0.00	0.10	0.30	0.60	0.65
Mg^{+2}	0.00	0.10	0.30	0.60	0.72
La^{+3}	0.00	0.00	0.00T	0.40	0.70E
Ce^{+4}	0.00	0.00T	0.00T	0.52	0.70T
Zr^{+4}	0.00	0.00	0.00T	0.00T	0-0.8
Th^{+4}	0.00T	0.00T	0.00T	0-0.7	0-0.8
U^{+6}	0.00T	0.00	0.50	0.70	0.75
V^{+4}	0.00	0.00	0.16	0.30	0.80
Be^{+2}	0.00T	0.20E	0.32	0.66	0.80
Tl^{+1}	0.00	0.05	0.30	0.56	0.72

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T A B L E - XXV

R_f values of metal ions in Iso-butyl alcohol-Formic acid systems.

System / Metal ions	IB_1	IB_2	IB_3	IB_4	IB_5
Ag^{+}	0.00	0.08	0.20	0.35	0.50
Hg^{+2}	0.00	-	0.51	0.60	0.65
Hg_2^{+2}	0.00T	0.25	0 & 0.50	0 & 0.50	0 & 0.40
Pb^{+2}	0.00	0.00			0.50
Cu^{+2}	0.00T	-	0.18	0.32	0.50
Cd^{+2}	0.00	0.10	0.10	0.12	0.60
Bi^{+3}	0.00	0.15	0.28	0.40	0.50
As^{+3}	0.18	0.30	0.20	0.20	0.12
Sn^{+2}	0.55	0.32	0.52	0.57	0.50
Sb^{+3}	0.60	0.40	0.50	0.63	0.52
Al^{+3}	0-0.18	0.10	0.20	0.60	0.77
Fe^{+3}	0.00T	0.10	0.30	0.44	0.70
Cr^{+3}	0.00	0.10	0.18	0.56	0.70
Mn^{+2}	0.00	0.08	0.20	0.40	0.70

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Co^{+2}	0.00	0.07	0.20	0.50	0.70
Ni^{+2}	0.00	0.08	0.20	0.51	0.75
Zn^{+2}	0.01	0.10	0.30	0.50	0.75
Ca^{+2}	0.00	0.05	0.18	0.45	0.70
Ba^{+2}	0.00	0.05	0.18	0.52	0.70
Sr^{+2}	0.00	0.08	0.20	0.47	0.72
Mg^{+2}	0.00	0.02	0.18	-	0.71
Be^{+2}	0.20	0.15	0.30	0.64	0.74
U^{+6}	0.00	0.12	0.30	0.40	0.60
Tl^{+}					
Th^{+4}	0.00	0-0.10	0-0.20	0-0.20	0-0.50
Zr^{+4}	0.00	0-0.16	0-0.30	0-0.50	0.70
Ce^{+4}	0.00	0.01	0.21	0 & 0.40	0.65
V^{+4}	-	0-0.15			
La^{+3}	0.00	0.05	0.24	0.56	0.70

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T A B L E - XXVI

R_f values of metal ions in Amyl-alcohol-Formic acid systems.

System / Metal ions	Am_1	Am_2	Am_3	Am_4	Am_5
Ag^{+}	0.00	0.03	0.00T	0.00T	0.00
Hg^{+2}	0.00 & 0.51	0.00 & 0.50	0.06	0.61	0-0.66
Hg_2^{++}	0.00T	0.00T	0 & 0.50	0.00 & 0.55	0.62
Pb^{+2}	0.00	0.02	0-0.25	0-0.23	0-0.52
Cu^{++}	0.00	0.15	0.22	0.30	0.62
Cd^{++}	0.00	0.10	0.30	0.15	0.60
Bi^{+3}	0.00T	0.13	0.24	0.50	0.50
As^{+3}	0.32	0.23	0.23	0.32	0.40
Sn^{++}	0.50	0.53	0.46	0.44	0.60
Sb^{+3}	0.50	0.52	0.55	0.60	0.55
Al^{+3}	0.00T	0.02	0.27	0.43	0.65
Fe^{+3}	0.00-S.F.	0-0.61	0.21	0.40	0.60
Cr^{+3}	0.00T	0.03	0.20	0.50	0.68
Mn^{+2}	0.00T	0.03	0.20	0.33	0.65

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Co^{++}	0.00	0.03	0.30	0.52	0.70
Ni^{++}	0.00	0.03	0.40	0.50	0.60
Zn^{++}	0.00	0.09	0.35	0.50	0.70
Ca^{++}	0.10	0.05	0.32	0.52	0.73
Ba^{++}	0.00	0.05	0.40	0.50	0.73
Sr^{++}	0.00	0.04	0.35	0.52	0.70
Mg^{++}	0.00	0.00	0.30	0.44	0.73
Be^{+2}	0.00-0.51	0.00	0.32	0.60	0.75
U^{+6}	0.00	0.03	0.28	0.47	0.66
Tl^{+}	0.00	0.00	0.35	0.60	0.68
Th^{+4}	0.00-0.50	0.00	0-0.25	0-0.42	0-0.70
Zr^{+4}	0.00	0.03	0-0.30	0-0.40	0-0.55
Ce^{+3}	0.09	0.10	0.26	0.44	0.53
V^{+4}	0.00	0.00	0.20	0.30	0-0.60
La^{+3}	0.00	0.00	0.28	0.44	0.73

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T A B L E - XXVII

R_f values of metal ions in Iso-amyl alcohol-Formic acid system.

Metal ions.	IAm_1	IAm_2	IAm_3	IAm_4	IAm_5
Ag^{+}	0.00	0.20	0.51	0.62	0.70
Hg^{+2}	0.00T	0-0.20	0.00T	0.60	-
Hg_2^{+2}	0.00	0.04	0.14	0-0.30	0-0.50
Pb^{+2}	0.00	0.10	0.33	0.52	0.70
Cu^{+2}	0.00	-	0.10	0.30	0.62
Cd^{+2}	0.00	0.09	0.30	0.35	0.70
Bi^{+3}	-	-	0.20	0.10	0.10
As^{+3}	-	-	-	-	-
Sn^{+2}	0.38	-	0.45	0.60	0.54
Sb^{+3}	0.00	0.20	0.31	0.50	0.70
Al^{+3}	0.00	0.10	0.30	0.40	0.72
Fe^{+3}	0.00	0.08	0.21	0.50	0.60
Cr^{+3}	0.00	0.12	0.20	0.40	0.56
Mn^{+2}	0.00	0.08	0.20	0.45	-

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Co^{+2}	0.00	0.10	0.25	0.54	0.72
Ni^{+2}	0.00	0.11	0.30	0.55	0.68
Zn^{+2}	0.00	0.08	0.30	0.46	0.70
Ca^{+2}	0.00	0.10	0.20	0.55	0.72
Ba^{+2}	0.00	0.07	0.31	0.54	0.67
Sr^{+2}	0.00	0.08	0.29	0.54	0.77
Mg^{+2}	0.00	-	0.26	0.54	0.64
Be^{+2}	0.00	0.09	0.28	0.45	0.50
U^{+6}					
Tl^{+}	0.00	0.00T	0-0.20	0-0.40	0-0.5
Th^{+4}	0.00	0.00T	0-0.2	0-0.4	0-0.5
Zr^{+4}	0.00	0.00T	0.00T	0-0.52	0-SF
Ce^{+4}	0.00	0.00T	0-0,2	0-0.3	0.56
V^{+4}	0.00	0.00T	0-0.3	0-0.40	0-SF
La^{+3}	0.00	0.00T	0.30	0.52	0.61

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T A B L E - XXVIII

Rf values of metal ions in Tert-Amyl alcohol-Formic acid systems.

System Metal ions.	T-Am$_1$	T-Am$_2$	T-Am$_3$	T-Am$_4$	T-Am$_5$
Ag^{+}	0.00	0.00T	-	-	0.00T
Hg^{+2}	0.00	0-0.30	0.32	0.00T	0.00
Hg_2^{+2}	0.00	0.00	0-0.40	0.05	0.60T
Pb^{+2}	0.00	0.00	0.15	0-0.40	0.50
Cu^{+2}	0.00	0.10	0.17	0.50	0.50
Cd^{++}	0.00	0.08	0.35	0.45	0.80
Bi^{+3}	0.00	0.10	0.12	0.20	0.80
As^{+3}	0.10	0.15	0.13	0.27	0.24
Sn^{+2}	0.52	0.53	0.50	0.60	0.55
Sb^{+3}	0.53T	0.55	0.50	0.52	0.50
Al^{+3}	0.00T	0.30E	0.32	0.60	0.70
Fe^{+3}	0.00	0.20	0.30	0.55	0.76
Cr^{+3}	0.00	0.02	0.30	0.50	0.70
Mn^{+2}	0.00	0.03	0.14	0.60	0.75

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Co^{++}	0.00	0.10	0.27	0.60	0.70
Ni^{++}	0.00	0.10	0.25	0.50	0.70
Zn^{++}	0.00	0.10	0.28	0.60	0.72
Ca^{++}	0.00	0.01	0.28	0.64	0.75
Ba^{++}	0.00	0.04	0.20	0.66	0.73
Sr^{++}	0.00	0.00	0.30	0 .56	0.71
Mg^{++}	0.00	0.05	0.30	0.55	0.70
Be^{++}	0.00T	0.30E	0.50	0.70	0.76
U^{+6}	0.00T	0.25	0.40	0.56	0.76
Tl^{+}	0.00	0-0.30	-	0.00T	0-0.70
Th^{+4}	0.00	0.00	0.00T	0.00T	0-0.80
Zr^{+4}					
Ce^{+3}	0.00	0.12	0-0.30	0-0.50	0-0.70
V^{+4}	0.00	0.08	0.10	0.40	0.80
La^{+3}	0.00	0.10	0-0.30	0-0.60	0.80

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T A B L E - XXIX

Rf values of metal ions octyl alcohol-Formic acid systems

System / Metal ions	O_1	O_2	O_3	O_4	O_5
Ag^{+2}	0.00	0.00T	0.00T	0.00T	0.00T
Hg^{+2}	0.00	0.00	0.20	0.47	0.70
Hg_2^{+2}	0.00	0.00	0.00T	0.00 & 0.30	0.80
Pb^{+2}	0.00	0.05	0.10	0.00 & 0.30	0-0.70
Cu^{+2}	0.00	0.05	0.10	0.22	0.77
Cd^{+2}	0.00	0.00	0.20	0.30	0.80
Bi^{+3}	0.00	0.05	0.05	0.30	0.73
As^{+3}	0.26	0.60	0.12	0.13	0.30
Sb^{+3}	0.25	0.29	0.43	0.35	0.44
Sn^{+2}	0.30	0.22	0.30	0.22	0.40
Fe^{+3}	0.00	0.00	0.05	0.42	0.81
Al^{+3}	0.00	0.10	0.09	0.32	0.73
Cr^{+3}	0.00	0.00	0.05	0.30	0.70
Zn^{+2}	0.00	0.00	0.18	0.30	0.80

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Mn^{+2}	0.00	0.05	0.05	0.28	0.81
Ni^{+2}	0.00	0.00	0.00	0.30	0.75
Co^{+2}	0.00	0.00	0.00	0.30	0.80
Ca^{+2}	0.00	0.00	0.20	0.40	0.75
Ba^{+2}	0.00	0.00	0.15	0.31	0.75
Sr^{+2}	0.00	0.00	0.18	0.29	0.73
Mg^{+2}	0.00	0.00	0.09	0.32	0.78
La^{+3}	0.00	0.00	0.05	0.35	0.75
Ce^{+4}	0.00	0.00	0.05	0.40	0.75
Zr^{+4}	0.00	0.00	0.00T	0-0.30	0.00T
U^{+6}	0.00	0.00	0.05	0.42	0.75
Th^{+4}	0.00	0.00	0.00T	0.00T	0.00T
Tl^{+}	0.00	0.05	0.12	0.40	0.80
Be^{+2}	0.00	0.00	0.05	0.43	0.80
V^{+4}	0.00	0.00	0.00	0.30	0.70

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T A B L E - XXX

Rf values of metal ions in Allyl alcohol-Formic acid systems.

System / Metal ions	A_1	A_2	A_3	A_4	A_5
Ag^{+}	0.00T	0.00T	0-0.60T	0.00	0.00
Hg^{+2}	0.00T	0.71	0.00 & 0.50	0.60	0.70
Hg_2^{+2}	0.00T	0.00	0.00	0.00	0.00 & 0.70
Pb^{+2}	0.00	0-0.20	0-0.20	0-0.60	0-0.70
Cu^{+2}	0.00	0.24	0.42	0.45	0.69
Cd^{+2}	0.00	0.36	0.40	0.67	0.68
Bi^{+3}	0.00	0.35	0.40	0.50	0.53
As^{+3}	0.46	0.41	0.42	0.40	0.40
Sn^{+2}	0.65C	0.67	0.57	0.55	0.52
Sb^{+3}	0.65T	0.63T	0.63	0.56	0.50
Al^{+3}	0.00T	0.41	0.57	0.50	0.80
Fe^{+3}	0.00	0.63E	0.60	0.65	0.80
Cr^{+3}	0.00	0.30	0.50	0.60	0.80

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Mn^{+2}	0.00	0.21	0.45	0.60	0.70
Co^{+2}	0.00	0.25	0.42	0.50	0.80
Ni^{+2}	0.00	0.20	0.41	0.61	0.80
Zn^{+2}	0.00	0.20	0.40	0.50	0.80
Ca^{+2}	0.00	0.20	0.40	0.52	0.70
Ba^{+2}	0.00	0.20	0.42	0.55	0.70
Sr^{+2}	0.00	0.22	0.41	0.60	0.75
Mg^{+2}	0.00	0.20	0.43	0.60	0.70
Be^{+2}	0.00T	0.15	0.40	0.60	0.82
U^{+6}	0.00	0.50	0.35	0.54	0.60
Tl^{+}	0.00	0.30	0.35	0.55	0.77
Th^{+4}	0.00T	0.00T	0-0.30	0-0.60	0.78
Zr^{+4}	0.00	0-0.40	0-0.40T	0-0.50	0-0.80
Ce^{+4}	0.00	0.25	0.32	0.50	0.80
V^{+4}	0.00	0.16	0.20	0.44	0.66
La^{+3}	0.00	0.30	0.50	0.60	0.81

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T A B L E - XXXI

Rf values of metal ions in Benzyl alcohol-Formic acid systems.

System / Metal ions.	B_{Z1}	B_{Z2}	B_{Z3}	B_{Z4}	B_{Z5}
Ag^{+}	0.00	0.00	0.00	0.00	0.00
Hg^{+2}	0.00	0.50	0.60	0.60	0.60
Hg_2^{+2}	0.00	0.00 & 0.50	0.60T	0.60	0.00 & 0.60
Pb^{+2}	0.00	0.08	0.31	0-0.30	0-0.60
Cu^{+2}	0.00	0.10	0.24	0.40	0.63
Cd^{+2}	0.00	0.16	0.30	0.45	0.80
Bi^{+3}	0.00	0.20	0.31	0.50	0.60
As^{+3}	0.40	0.44	0.34	0.32	0.28
Sb^{+3}	0.26	0.42	0.60	0.56	0.53
Sn^{+2}	0.40	0.45	0.60	0.50	0.60
Fe^{+3}	0.05	0.31	0.40	0.50	0.75
Al^{+3}	0.08	0.10	0.20	0.52	0.85
Cr^{+3}	0.00	0.08	0.21	0.50	0.75

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Zn^{+2}	0.05	0.10	0.21	0.60	0.86
Mn^{+2}	0.00	0.08	0.21	0.55	0.76
Ni^{+2}	0.00	0.08	0.17	0.54	0.80
Co^{+2}	0.00	0.06	0.22	0.60	0.80
Ca^{+2}	0.00	0.10	0.25	0.60	0.88
Ba^{+2}	0.00	0.10	0.28	0.68	0.85
Sr^{+2}	0.00	0.09	0.27	0.50	0.85
Mg^{+2}	0.00	0.10	0.20	0.70	0.80
La^{+3}	0.00	0.08	0.27	0.54	0.80
Ce^{+4}	0.08	0.08	0.21	0.55	0.75
Zr^{+4}	0.00	0.00	0.00T	0-0.70	0-0.70
U^{+6}	0.10	0.15	0.30	0.66	0.80
Th^{+4}	0.00	0.08	0-0.30	0-0.50	0-0.70
Tl^{+}	0.00	0.18	0.32	0.64	0.80
Be^{+2}	0.05	0.10	0.30	0.70	0.85
V^{+4}	0.00	0.00	0.22	0.50	0.70

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T A B L E - XXXII

Rf values of metal ions in cyclohexanol-Formic acid systems.

Systems / Metal ions.	C_1	C_2	C_3	C_4	C_5
Ag^{+}	0.00	0.00	0.00	0.00T	0.00
Hg^{+2}	0.00T	0.00T	0.62T	0.60	0.71
Hg_2^{+2}	0.00	0.00T	0.00 & 0.60	0.00 & 0.50	0.00 & 0.60
Pb^{+2}	0.00	0.18	0-0.20	0.38	0.00 & 0.50
Cu^{+2}	0.00	0.10	0.10	0.40	0.52
Cd^{+2}	0.02	0.10	0.25	0.45	0.70
Bi^{+3}	0.00	0.20E	0.30	0.32	0.60
As^{+3}	0.30	0.15	0.52	0.33	0.37
Sn^{+2}	0.57	0.61	0.65	0.60	0.57
Sb^{+3}	0.63	0.66	0.62	0.63	0.62
Fe^{+3}	0.00	0.14E	0.30	0.62	0.73
Al^{+3}	0.09	0-0.2	0.16	0.53	0.70
Cr^{+3}	0.00	0.00T	0.20	0.50	0.65

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Mn^{+2}	0.00	0.08	0.14	0.42	0.70
Zn^{+2}	0.00	0.10	0.20	0.57	0.68
Ni^{+2}	0.00	0.08	0.22	0.46	0.67
Co^{+2}	0.00	0.08	0.20	0.51	0.71
Ca^{+2}	0.00	0.00	0.10	0.50	0.70
Ba^{+2}	0.00	0.05	0.12	0.51	0.76
Sr^{+2}	0.00	0.00	0.20	0.42	0.72
Mg^{+2}	0.00	0.00	0.10	0.50	0.75
La^{+3}	0.00	0.06	0.15	0.62T	0.71
Ce^{+4}	0.00T	0.08	0.13	0.51	0-0.55
Zr^{+4}	0.00	0.00	0.00T	0.60TD	0-0.70
Th^{+4}	0.00T	0.05	0.10	0-0.60	0-0.70
U^{+6}	0.00	0.18E	0.25	0.53	0.71
V^{+4}	0.00	0.00	0.10	0-0.40	0.60
Be^{+2}	0.10	0.20T	0.22	0.52	0.80
Tl^{+}	0.00	0.12	0.20	0.60	0.71

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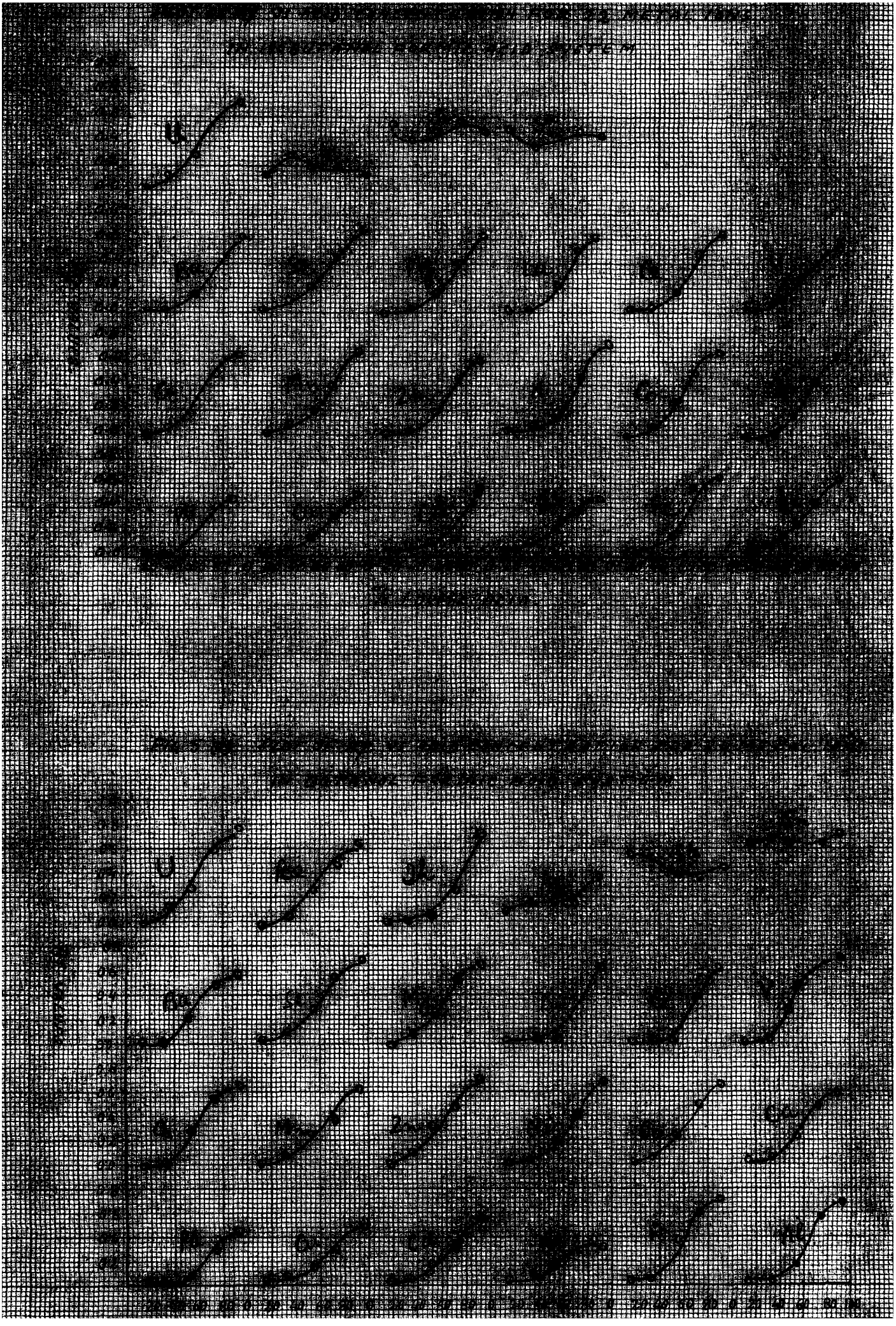
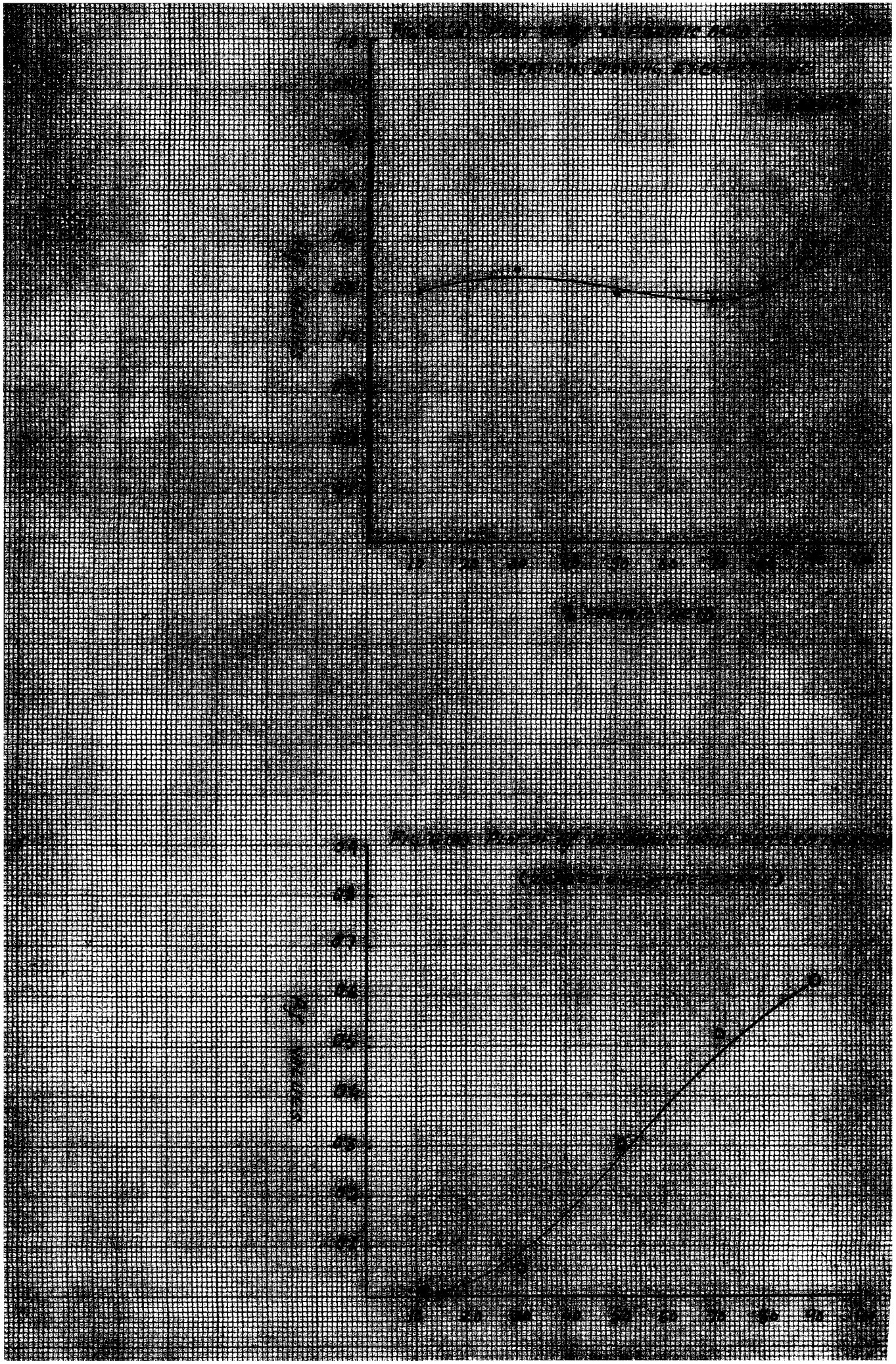
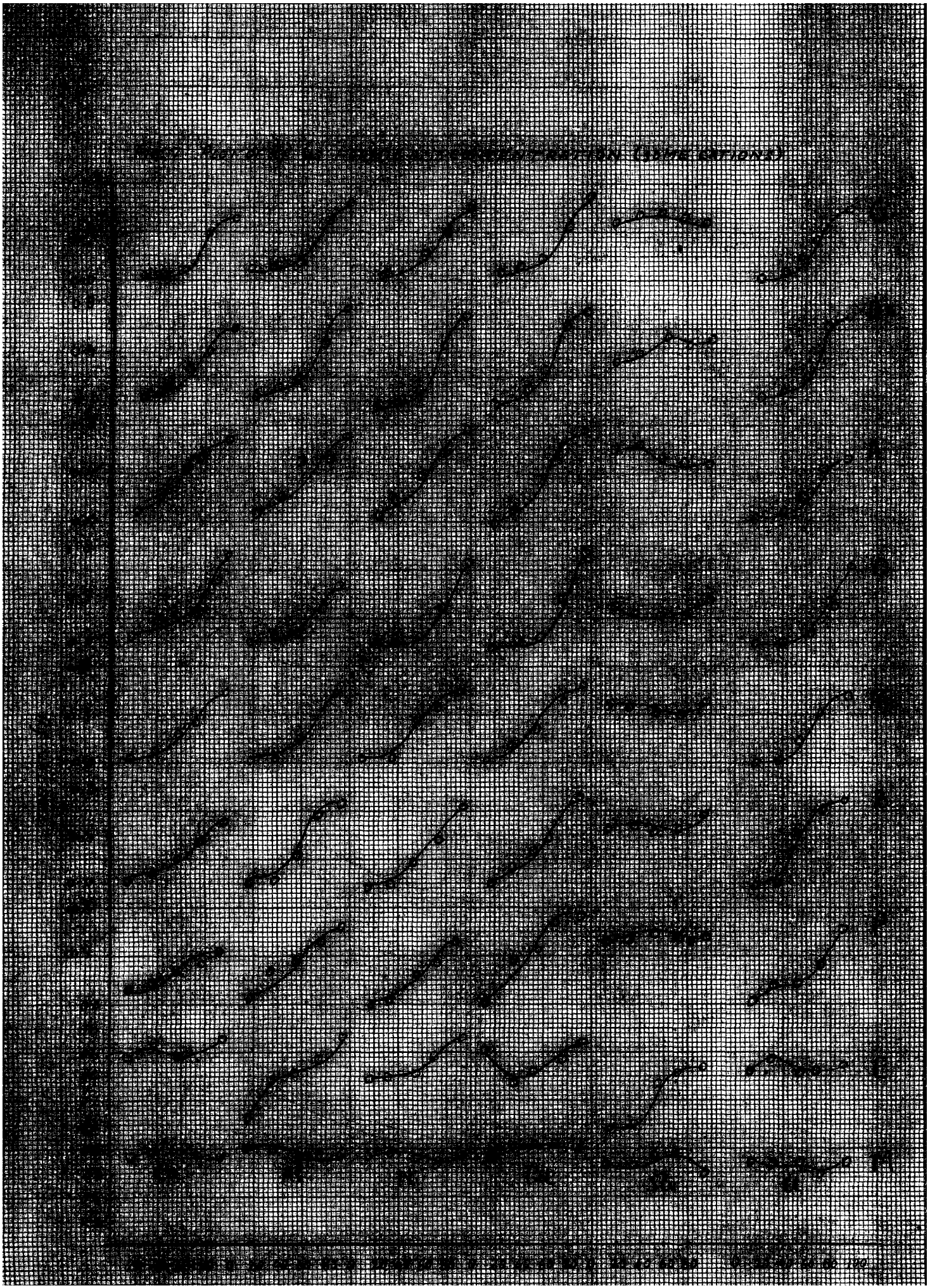
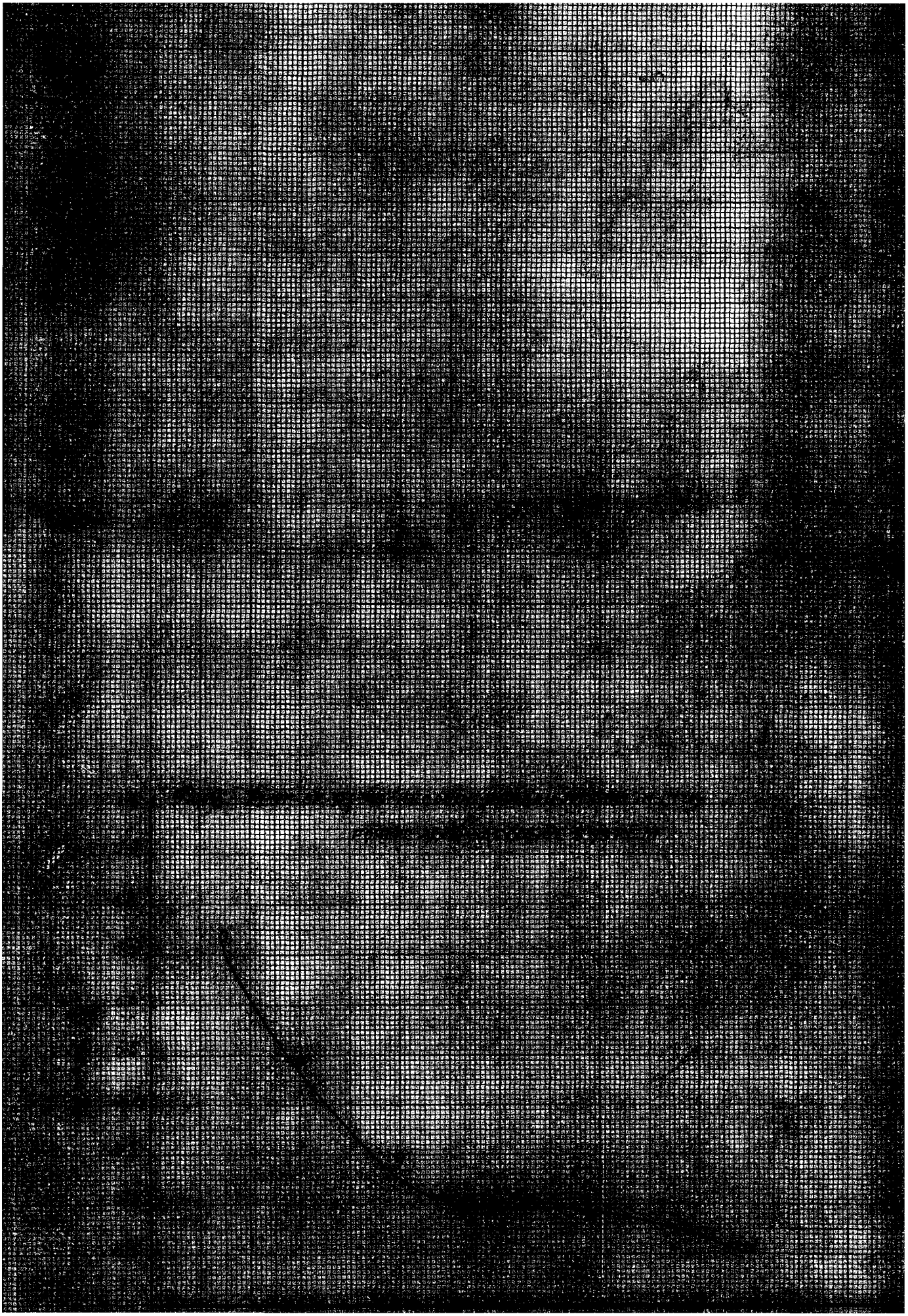




D I S C U S S I O N

A representative curve of R_f values Vs formic acid concentration is shown in Figure 6. Figure 6(a) refers to most metal ions. At low formic acid concentrations there is only slight migration on paper. This is easily explained by the small polarity of the solvent systems. As the concentration of formic acid increases the migration of the cations also increases to some extent. The full effect of the polarity of the solvent system is not felt as the polar character of the stationary phases (paper) retards the movement of the ions significantly. When the formic acid concentration is sufficiently high i.e. 30% or higher, Rf values increase much more abruptly since the solvent system is now sufficiently polar to overcome considerably the retarding influence of the stationary phase. When the formic acid concentration is 70%, the system is now so polar that any further increase in the acid concentration does not result in a corresponding increase in Rf values. The resulting curve is therefore S shaped.





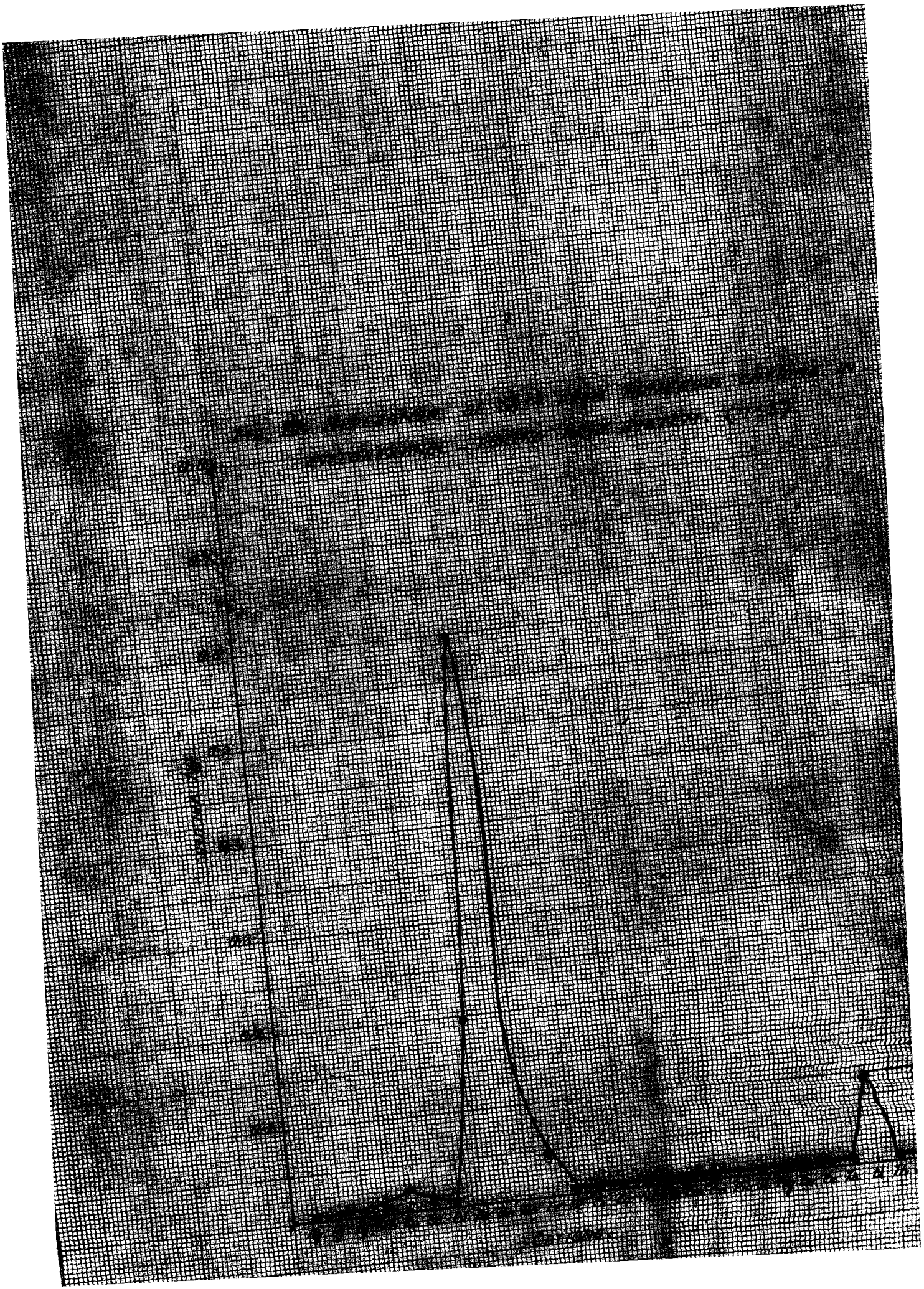


Figure 6(b) refers to the behavior of Sn^{+2} and Sb^{+3}. These ions show some unusual characteristics. Thus even in low formic acid concentrations their Rf values are very high. The second interesting point is that their Rf values appear to be independent of the formic acid concentrations. This behavior may be explained on the assumption that the partition coefficient of the antimony-formic acid complex is independent of the formic acid concentration if it varies from 10% to 90%. A plot of Rf Vs % of formic acid does not give an S shaped curve in the case of methanol since methanol itself is a very polar substance and the change in concentration of formic acid does not significantly effect the polarity of the system. The plot of Rf Vs number of C atoms also gives an S shaped curve in the reverse sense i.e. the Rf value is initially high and then gradually decreases Fig.8. This follows from the fact that the polarity of the alcohol decreases with increase in chain length. Figures 9 and 10 show that tin and antimony can be separated from numerous metal ions. Separation of binary mixtures containing either tin or antimony with one of the cations chromatographed was also successful. However Hg_2^{+2} and Fe^{+3} interfered.

Some other interesting features may also be noted. When n propanol is replaced by an unsaturated alcohol e.g. allyl alcohol the Rf values increase in most cases due to the increased polarity of the sytem. The higher Rf values of metal ions in branched chain alcohols when compared with normal alcohols may also be explained similarly.

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C H A P T E R - VI

Precipitation Chromatography on Strontium Chromate Paper.

Recently there has been renewed interest in the precipitation chromatography since it needs only simple amd inexpensive equipment and can be used for rapid semi-quantitative determinations of numerous metal ions. Manganese ferrocyanide (10), ferric hydroxide (13), sodium thiosulphate (9), hydroxyl amine (7), aluminum hydroxide (4), nickel ferrocyanide (2), ammonium nitrate (1), ammonium phosphomolybdate (11), potassium iodide-sodium hypophosphite (12) and cadmium sulphide (3) have been utilized for some studies on Ag^{+}, [illegible], Pb^{+2}, Cd^{+2}, Cu^{+2}, As^{+3}, Sb^{+3}, Sn^{+2}, Bi^{+3}, Ni^{+2}, Co^{+2}, Zn^{+2}, UO_2^{+2}, Th^{+4}, Ir^{+4}, Rh^{+3}, Pd^{+2}, Hg^{+2}, Rb^{136}, Cs^{134}, Sr^{89}, Y^{91} and Radionuclides.

However, chromates have not been systematically studied as precipitants although they form a large number of insoluble compounds with metal ions. Potassium chromate has been used to study the chromatographic movement of some cations and to investigate the solubility

of chromates (8). Liimatta and coworkers showed that it is possible to determine Ag^{+}, Cu^{+2}, Fe^{+3}, Hg^{+2}, Co^{+2}, Ni^{+2}, Zn^{+2} and Cd^{+2} by precipitation chromatography (10). No studies have been recorded for the quantitative determination of Ag^{+} and Hg_2^{+2} using chromate as precipitant.

We therefore investigated the behavior of thirty cations on strontium chromate impregnated paper and found that mercurous and silver can be easily separated from numerous cations, and they can also be quantitatively determined using the rather simple technique of precipitation chromatography.

E X P E R I M E N T A L

Reagents and Apparatus: Spot solutions described in Chapter II were used. Silver and mercurous nitrates were standardized volumetrically for quantitative determinations. A planimeter was used to measure the spot area.

Preparation of Paper: 0.2 Molar solution of strontium nitrate was prepared and its pH fixed between 7 & 8. Whatman No.1 circles of diameter 7 cms. were dipped in this solution and excess of the liquid was soaked in paper

cuttings. Later the circles were dried in an oven at 70°C. These papers were then kept in 0.2 M solution of potassium chromate for about five minutes. After the complete pptn . of strontium chromate on paper it was dried, washed with water and redried in the oven. Reverse process was found to be less efficient.

Spotting: A single spot with a thin glass capillary was applied for qualitative studies. For quantitative determinations 0.005 ml of the cation solution under study was applied with a micropipette.

Development: Simple capillary analysis described by Spain (10) was adopted. The cations under study were spotted in the center of paper circles which was previously marked. The circle was kept on the lid of a petridish and carefully covered with a short stemmed funnel. Glass capillaries with fore-end drawn were used as feed-ers. The capillary was dipped into the developing solution and was kept into the center of the paper. The whole chromatographic process took about twenty minutes. 0.2 M strontium nitrate and 10% ammonium hydroxide were used as developers. Standard detectors described in Chapter II were used.

R E S U L T S

Various cations were developed with 0.2 M strontium nitrate solution at pH 6 and 10% ammonium hydroxide solution. Results are summarized in Table XXXIII.

T A B L E - XXXIII

Rf values of cations in 0.2 M strontium nitrate and 10% ammonium hydroxide.

Cations	$Sr(NO_3)_2$	NH_4OH	Cations	$Sr(NO_3)_2$	NH_4OH
Ag^{+}	0.00	S.F.	Fe^{+3}	0.00	0.00
Hg_2^{+2}	0.00	0.00	Al^{+3}	0.00	0.00
Pb^{+2}	0.00	0.00	Cr^{+3}	0.00	0.00
Hg^{+2}	0.00	0.00	Mn^{+2}	0.00	0.00
Cu^{+2}	0.70	0.41	Co^{+2}	S.F.	0.00
Cd^{+2}	S.F.	0.00	Ni^{+2}	S.F.	S.F.
Bi^{+3}	0.00	0.00	Zn^{+2}	0.00	0.00
As^{+3}	0.00	0.00	Ca^{+2}	0.00	0.00
Sb^{+3}	0.00	0.00	Ba^{+2}	0.00	0.00
Sn^{+2}	0.00	0.00	Mg^{+2}	0.00	0.00
La^{+3}	S.F.	0.00	Ce^{+3}	0-S.F.	0.00

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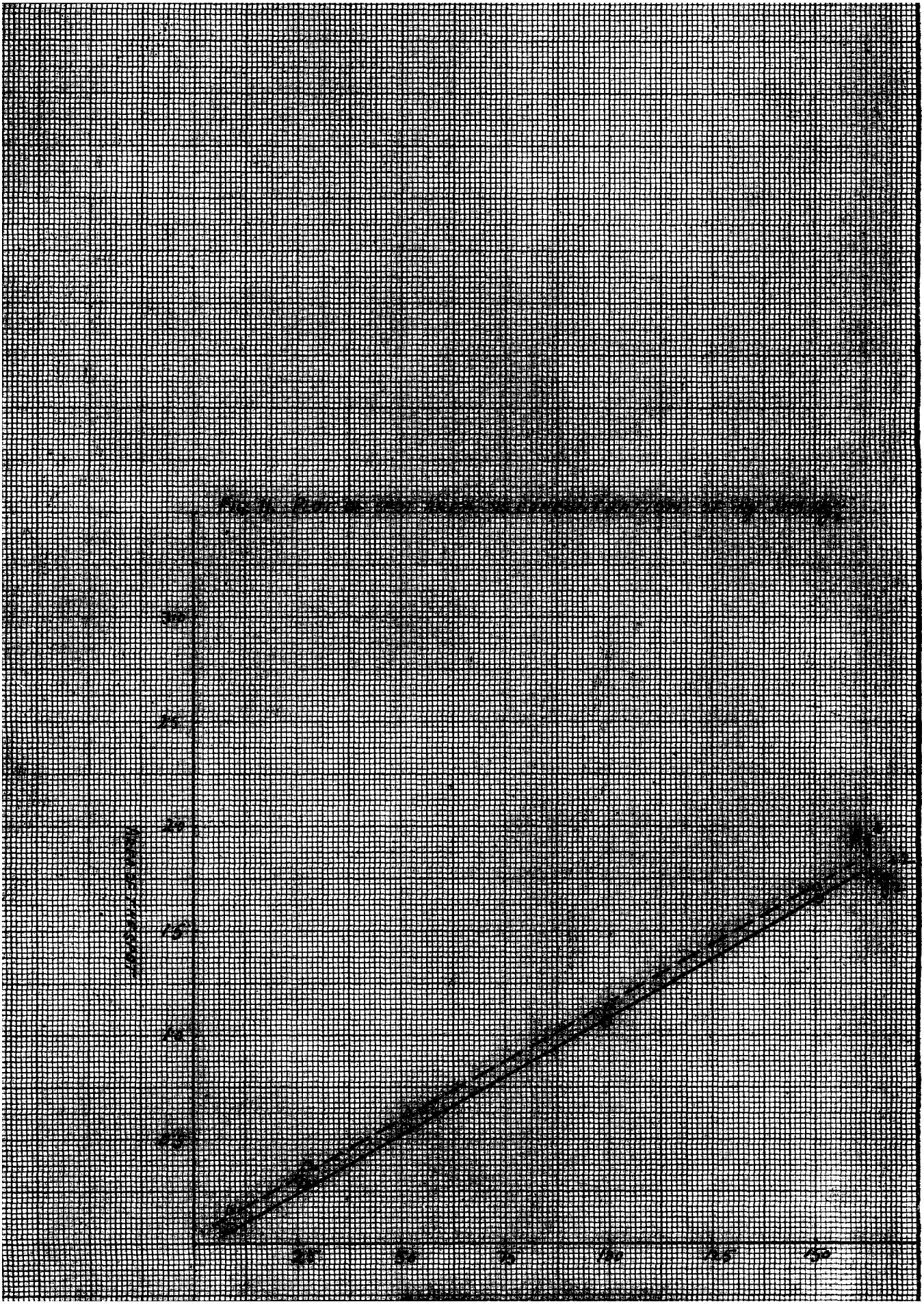
Temperature Fahrenheit
30°
25°
20°
15°
10°
5°
0°
-5°
-10°
-15°
-20°
-25°
-30°
-35°
-40°
-45°
-50°
-55°
-60°
-65°
-70°
-75°
-80°
-85°
-90°
-95°
-100°
-105°
-110°
-115°
-120°
-125°
-130°
-135°
-140°
-145°
-150°
-155°
-160°
-165°
-170°
-175°
-180°
-185°
-190°
-195°
-200°

V^{+4}	0.00	0.00	UO_2^{+2}	0.00	0.00
Be^{+2}	0.00	0.00	Th^{+4}	0.00	0.00
Au^{+3}	0.00	0.00	Y^{+3}	0.00 & S.F.	0.00
Ti^{+4}	0.00	0.00	Zr^{+4}	0.00	0.00

A number of binary and ternary mixtures were resolved with the help of these systems. Development with strontium nitrate separates the following mixtures: Cu^{+2}, Co^{+2} (0.68 & 0.90); Cd^{+2}, Cu^{+2} (1.00 & 0.70); Cd^{+2} As^{+3} (1.00 & 0.00); Cu^{+2}, Ni^{+2} (0.70 and 0.92); Bi^{+3}, Cu^{+2}, Cd^{+2} (0.00, 0.70 and 1.0); Pb^{+2}, Cu^{+2} and Cd^{+2} (0.00, 0.70 and 1.0). Mixtures separated with ammonium hydroxide were: Ag^{+}, Cu^{+2}, Hg_2^{+2} (1.00, 0.30 and 0.00); Ag^{+2}, Cu^{+2}, Pb^{+2} (1.0, 0.30 and 0.00) and Ni^{+2}, Cu^{+2}, Co^{+2} (1.00, 0.30 and 0.00). R_f values are shown in brackets.

Papers impregnated with strontium carbonate alone and with a mixture of strontium carbonate and strontium chromate were also used for similar studies, but no improvement in the results was obtained.

5 to 150 micrograms of Ag^{+} and Hg_2^{+2} were spotted and the plot of spot area Vs concentrations is shown in Figure 11.

D I S C U S S I O N

The principle of precipitation chromatography is delightfully simple. Let us suppose that we are using strontium chromate paper and we wish to study the behavior of lead ions with strontium nitrate as an eluent. The solubility product of lead chromate and strontium chromate are 5.8×10^{-6} and 1.8×10^{-1} (Compare Table XXXIV). The lead ions are distributed between the stationary phase (strontium chromate) and the mobile phase (strontium nitrate) since the solubility product of lead chromate is comparatively very small the reaction,

$$Sr\ CrO_4 + Pb^{+2} \rightleftharpoons PbCrO_4 + Sr^{++}$$

goes towards the right and the Rf value of Pb^{+2} is zero which is retained as lead chromate at the point of application.

A similar explanation may be advanced to explain the behavior of silver ions using ammonium hydroxide as an eluent. This results in the formation of $Ag(NH_3)_2^+$ complex. This does not exchange significantly with strontium ions since $Ag\ (NH_3)_2^+$ probably does not form an insoluble chromate. The solubility product of copper chromate is slightly smaller than that of strontium chromate. Hence the

Cu^{+2} ions are neither retained entirely at the point of application nor they migrate completely to the solvent front. The R_f values are therefore 0.40 - 0.70.

T A B L E - XXXIV

Solubility of some chromates (5,6).

Metal ion	Solubility in gms/100 gms of water.	Metal ion	Solubility in gms/100 gms of water.
Ag^{+}	2.6×10^{-3}	Zn^{+2}	Ins.
Pb^{+2}	5.8×10^{-6}	Co^{+2}	Ins.
Hg_2^{+2}	V.Sl.S.	Ba^{+2}	3.7×10^{-4}
Bi^{+3}	8.5×10^{-5}	Sr^{+2}	1.8×10^{-1}
Cd^{+2}	Ins.	Mg^{+2}	V.S.
Sn^{+4}	S	Cu^{+2}	1.9×10^{-3}
Sn^{+2}	Sl.S.	Tl^{+}	6.2×10^{-5}
La^{+3}	0.02	Al^{+3}	W
Ce^{+3}	Ins.	Cr^{+3}	A
Fe^{+3}	W	Th^{+4}	Ins.
UO_2^{+2}	V.S.	Y^{+3}	S
Ni^{+2}	A		

Ins. Insoluble. S: soluble, W: soluble in water, V.Sl.S: Very slightly soluble. A. Soluble in acid

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C H A P T E R - VII

Distribution Coefficient of Antimony in Anisole-Formic acid system.

Liquid liquid extraction is a convenient method for the separation and determination of inorganic elements in complex mixtures. Radiotracers offer simple and rapid methods of analysis for the species extracted. Applications of various extractors for the determination of antimony is summarized in Table XXXV. A reference to this table shows that no studies have been reported of the extraction of Sb and Sn in anisole from formic acid systems. Our studies on the separation of Sn and Sb had shown that anisole-formic acid system is v-ery efficient for the separation of Sn and Sb. If we could find out the distribution coefficients of Sn and Sb in anisole-aqueous formic acid systems this may help in the correlation of Rf values with the distribution coefficient and it may give us a new pair of solvent systems for the extraction of tin and antimony. The present work was therefore undertaken to determine the distribution

coefficients of tin and antimony in anisole-formic acid systems. The tracer technique was used in these studies since it is simple, fast and elegant.

T A B L E - XXXV

L - L Extraction of Antimony and Tin.

Element extracted.	Separation From	Aqueous phase	Organic Phase	Reference
Sb	Mo	Citric acid Methyl Violet	Benzene, Toluene	(16)
	Many cations	4-11M HCl	T.B.P.	(28)
		HCl-Brilliant green	Benzene	(15)
		HCl	Isopropyl ether	(36)
	Fission products	7M HCl-6M H_3PO_4	Diisobutyl carbinol-n Heptane	(17)
		Ph_2Methyl Fluorone	M1 BK Ethylacetate Butyl acetate 4-Methyl 2-Pentanol	(20)
	Mg Alloys	Na-Diethyl dithiocarbamate	Carbon Tetra chloride	(35)
		7M HCl	Isobutyl acetate Bisisobutyl Carbinol	(14),(17) (29)

... Contd. on next page ...

		6M HCl-Rhodamine-B	Carbon Tetra Chloride Chlorobenzene	(9),(24), (32)
		6M HCl-$NaNO_2$	Brilliant green Toluene	(1),(31)
		KI, K_2SO_4 or HCl	M I B K	(7)
	As,Bi	H_2SO_4, KI	M I B K	(33)
	Many Metals	HCl diff conc.	Ethyl acetate	(12)
		"	T.B.P.	(25)
		"	M I B K	(8)
		H_2SO_4, $HClO_4$	Benzene	(26)
	Many cations	1-2M HCl	Ethyl acetate	(40)
	Tl-Ir	H_2SO_4, Cupferron	Chloroform	(18)
	Many cations	pH 9.2 EDTA-NaCN	Sod. diethyl dithio carbamate chloroform	(2)
		9N H_2SO_4 KI	Benzene	(39)
	W,V,Fe	3-6M HCl	"	(19),(23), (38)
Sn	Zn	HCl-Amm. Acetate	Carbontetra chloride	(3)
	Many Elements	HCl	Tris(2-ethyl Hexyl) phosphene oxide in cyclohexane	(27)

... Contd. on next page ...

Most Elements	$HClO_4$, NaI, $NaClO_4$	Benzene	(6)
Soil	HCl, SCN ascorbic acid	Ethyl acetate	(22)
Fe	HCl, Ascorbic acid	M I B K	(37)
Nuclear Reactor	pH 0.8, 20% NH_4Cl 8-Quinonol	Chloroform	(4)
	Alizarine Blue, N HCl	Cyclohexanone Ethylacetate	(10)
In-Sb	4M HI, KI, H_2SO_4	Ether	(14)
Pb	7-8 M HCl	Amberlite LA2/ Xylene	(21)
Sb	H_2SO_4, NH_4CN	Ethyl acetate	(34)
	IM HNO_3	Butyl phosphoric acid Butyl ether	(30)
Many Metals	4.6M HF	Ethyl ether	(13)
	6.9M HI	Ethyl ether	"
	KI-1.5M H_2SO_4	"	(11)
	pH 2.5-6	8-Quinonol in Chloroform	(5)

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E X P E R I M E N T A L

Reagents: Antimony-125 trichloride was obtained from Atomic Energy Establishment Bombay. Ten ml of solution contained 540 microcuries. E. Merck hydrochloric acid and formic acid were used. Anisole (Bush) was distilled before use.

Apparatus: The radiotracer was measured with a micro-pipette and the separation of the layers was performed in 50 ml separating funnels. β-emission was measured from a counter. Supplied by A.E.E. Bombay. Planchets of diameter 2 cms with a cavity of diameter 1 cm were kept on an aluminium plate which was inserted in the counter.

Rubber gloves were used to avoid the contact of radio active material with the skin. Cellotape was used to cover the planchets. Standardization of antimony and hydrochloric acid solutions was made with sodium hydroxide and potassium permanganate solutions.

R E S U L T S

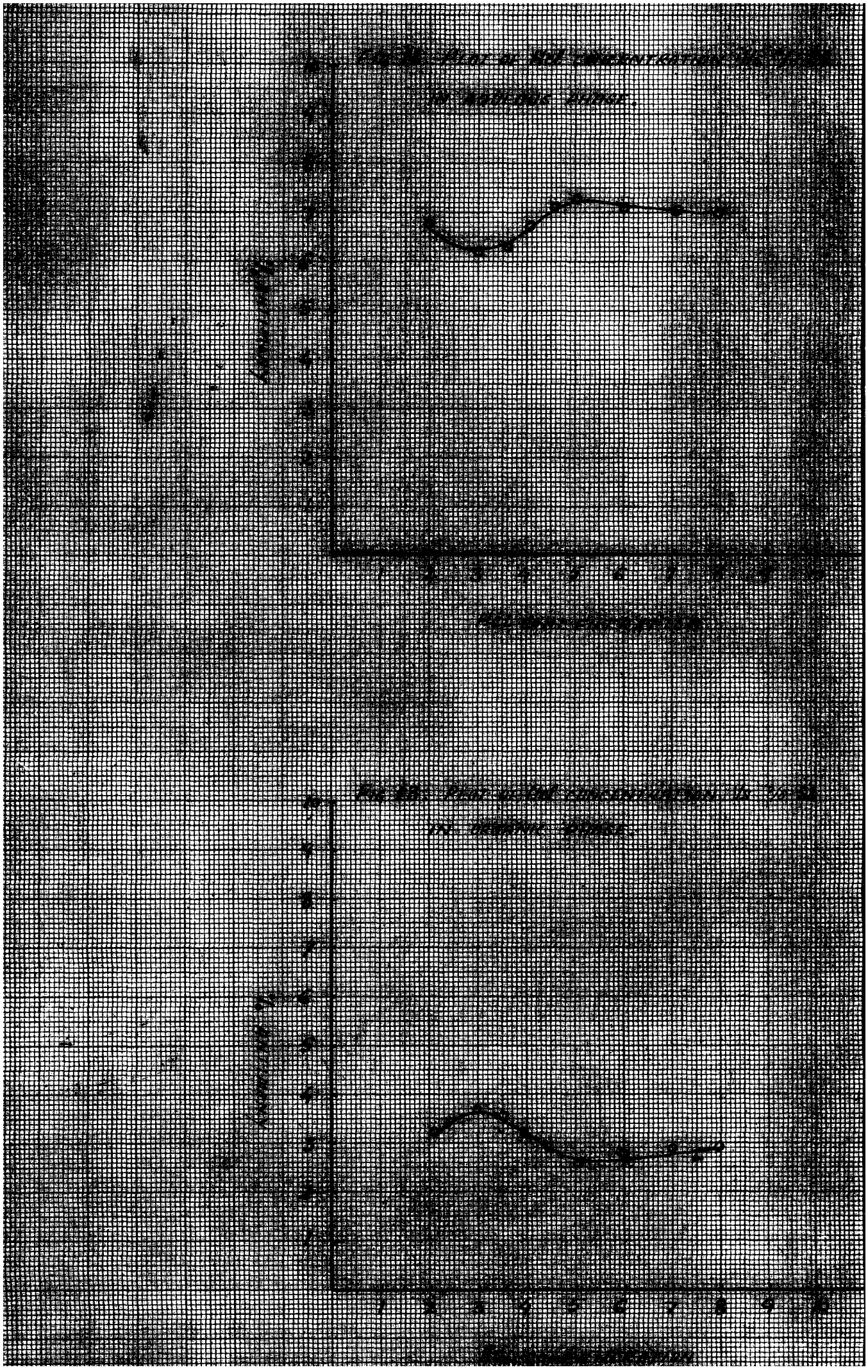
Measured quantities of hydrochloric acid were added to the anisole-formic acid (1:1) mixture, to study the separation of layers. Almost equal layers of the organic and aqueous phases were formed when 14 ml of anisole-formic acid (1:1) were mixed with 1 ml of hydrochloric acid . 0.1 M solutions of antimony trichloride in hydrochloric acid ranging from 3 - 8 M were prepared. 1 Ml of each solution was shaken with 15 ml of anisole-formic acid mixture and 0.1 ml of isotope solution. On attainment of the equilibrium 0.1 ml portions of the liquids from the aqueous and organic phases were taken out, poured in the clean planchets, dried with a lamp and subjected to β counting. Results are recorded in Table XXXVI.

T A B L E - XXXVI

Distribution of antimony in hydrochloric acid-anisole-formic acid system.

Strength of HCl	Counts in aq.phase.	Counts in organic phase	% of Sb organic phase.	% of Sb aq.phase
3 M	338	222	39.8	60.2
4 M	301	220	42.2	57.8
6 M	460	261	36.2	63.8
8 M	462	210	31.2	68.8

A more detailed study was performed to confirm the fact that 3 or 4 M hydrochloric acid gives highest percentage of antimony in organic phase. Nine samples of hydrochloric acid (2-8 M) were prepared. Strength of antimony was fixed at 0.2 M and 0.5 ml of hydrochloric acid with antimony was added to 7 ml (1:1) mixture of anisole-formic acid. 0.1 ml of the radiotracer was added and 0.1 ml portions of the separated layers were taken out for the β counting. Results are summarized in Table XXXVII.



T A B L E - XXXVII

Distribution of antimony in 7 ml anisole formic acid and 0.5 ml hydrochloric acid.

Strength of HCl	Counts in aqueous phase /2 mnts.	Counts in organic phase /2 mnts.	% of antimony Organic Phase	Aq.phase
2 M	1998	948	31.8	68.2
3 M	1366	826	37.6	62.4
3.5 M	1680	999	36.8	63.2
4 M	1566	766	32.5	67.5
4.5 M	1723	745	30.0	70.0
5 M	1933	686	25.6	74.4
6 M	1877	733	27.9	72.1
7 M	1784	746	28.9	71.1
8 M	1683	748	30.6	69.4

Background counts in Tables XXXVI and XXXVII were 32 and 40 per two minutes respectively.

Results of these tables were plotted in Figures 12 and 13.

D I S C U S S I O N

A reference to table XII shows that antimony is extracted to a considerable extent by the organic phase. The concentration of antimony in the organic phase depends to some extent on the concentration of hydrochloric acid originally present in the antimony sample. About 3 M hydrochloric acid is best for the maximum extraction of antimony in the organic phase. Similar experiments with Sn^{+2} will be required before the Rf values of Sn^{+2} and Sb^{+3} in anisole-formic acid systems can be correlated with the distribution coefficient.

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Paper chromatography of Sn^{2+} and Sb^{3+}

Sn^{2+} and Sb^{3+} are rather difficult to separate by paper chromatography[1] and very few good separations[2] of these cations have been reported. The separations obtained by HARASAWA[3] and STEFANOVIĆ *et al.*[4] could not be confirmed by LEDERER[1] or by us. The paper chromatography of these cations was therefore studied more exhaustively. As a result some good separations have been developed.

Some of the solvents tried were: propionic acid, butyric acid, isovaleric acid, palmitoyl chloride, acetyl chloride, acetic anhydride, aniline, diethylamine, methylcyclohexanone, anisole, aliphatic alcohols, acetaldehyde, formaldehyde, quinoline,

TABLE I

ASCENDING CHROMATOGRAPHY

	Solvent	R_F		Time h
		Sn^{2+}	Sb^{3+}	
1	*Formic acid–anisole (1:1)	0.26	0.54	2
2	Formic acid–anisole (1:2)	0.14	0.44	2
3	Acetic acid–formic acid (1:1)	0.33	0.47	2
4	Acetic acid–formic acid (1:2)	0.42	0.53	2
5	Formic acid–butyric acid (1:1)	0.36	0.52	2
6	Formic acid–propionic acid (1:1)	0.19	0.41	2
7	Formic acid–propionic acid (1:2)	0.16	0.40	2

TABLE II

DESCENDING CHROMATOGRAPHY

	Solvent	R_F		Time h
		Sn^{2+}	Sb^{3+}	
1	*Formic acid–anisole (1:1)	0.14	0.50	2
2	Acetic acid–formic acid (1:2)	0.39	0.47	2
3	Formic acid–butyric acid (1:1)	0.31	0.46	2
4	Formic acid–propionic acid (1:1)	0.33	0.48	2

TABLE III

CIRCULAR CHROMATOGRAPHY

	Solvent	R_R		Time min
		Sn^{2+}	Sb^{3+}	
1	*Formic acid–anisole (1:1)	0.39	0.67	20
2	Acetic acid–formic acid (1:2)	0.53	0.67	20
3	Formic acid–butyric acid (1:1)	0.33	0.53	20
4	Formic acid–propionic acid (1:1)	0.36	0.62	20

2,4-hexanedione, lactic acid and 10% solutions of urea, thiourea, succinic acid, tartaric acid, citric acid, ammonium chloride, sodium chloride, potassium chloride and sodium bisulphite.

Papers impregnated with the following organic and inorganic adsorbents were also used: ammonium oxalate, ammonium carbonate, glucose, naphthalene, benzoic acid and sodium chloride.

The successful separations are given in Tables I, II and III. The systems that gave the best results are marked with an asterisk.

In order to find out whether the separations can be of use in qualitative analysis $M/5$ test solutions of $SnCl_2$ and $SbCl_3$ were mixed in different ratios and separated by ascending chromatography using a mixture of anisole and formic acid (1:1) as the developer. In all cases good separations were obtained. The papers were conditioned for 1 hour prior to chromatography. The results are summarized in Table IV.

TABLE IV

SEPARATION OF MIXTURES OF Sn^{2+} AND Sb^{3+} OF VARYING COMPOSITION

Ratio of $SnCl_2$:$SbCl_3$	R_F		*Time of development* h
	Sn^{2+}	Sb^{3+}	
2:1	0.18	0.54	1
3:1	0.19	0.51	1
4:1	0.22	0.53	1
1:2	0.10	0.48	1
1:3	0.17	0.61	1
1:4	0.17	0.52	1

The test solutions were diluted to $M/50$ and $M/100$. When these solutions were spotted and developed with anisole–formic acid (1:1), after conditioning for one hour, good separations were obtained. The results are summarised in Table V.

TABLE V

SEPARATION OF Sn^{2+} AND Sb^{3+} AT HIGHER DILUTIONS (ASCENDING TECHNIQUE)

Concn. of test solution	R_F		*Time of development* h
	Sn^{2+}	Sb^{3+}	
$M/50$	0.06	0.38	1
$M/100$	0.01	0.36	1

The zones of Sn^{2+} were always compact, well defined and well separated, while the zones of Sb^{3+} were sometimes a little diffuse.

On repeating the separation reported by STEFANOVIĆ *et al.*[4] it was found that besides being time-consuming (21 hours) their method is not reproducible. Similarly the separation advocated by HARASAWA[3] fails under the conditions specified. It is possible that in our separations formic acid plays a beneficial role by preventing the oxidation of Sn^{2+} and Sb^{3+} to higher valence states.

Butyric acid commercial 50% (E. Merck) and anisole, free from alcohol (Naarden), were used. All the other chemicals were of reagent grade, either from E. Merck, or British Drug Houses. Schleicher & Schüll No. 2043a sheets were used for ascending and descending chromatography. Whatman No. 1 filter paper circles (diameter 12.5

cm) were used with the Kawerau apparatus. The $M/5$ test solutions of $SnCl_2$ and $SbCl_3$ for the experiments given in Tables I–IV were prepared as follows.

1.89 g of $SnCl_2$ and 2.28 g of $SbCl_3$ crystals were dissolved in 15 ml of conc. HCl separately and the solutions were then diluted to 50 ml with distilled water. The $M/50$ and $M/100$ test solutions were prepared by subsequent dilution with 30% HCl. Two spots (approx. 0.0014 ml) of each of the two test solutions were applied to the test paper with a thin glass capillary. The cations were detected by hydrogen sulphide gas. The room temperature was 28° ± 4°.

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Paper Chromatography of Metal Ions in Formic Acid-alcohol Systems: Separation of Tin and Antimony from Numerous Metal Ions*

Mohsin Qureshi and Mukhtar A. Khan

Chromatographic behaviour of 29 common cations has been studied in alcohol-formic acid ratios of 9:1, 7:3, 5:5, 3:7, and 1:9. The plot of R_f value of a metal ion against %formic acid provides an S-shaped curve, the R_f value increasing with increase in the acid concentration.

Sn^{2+} and Sb^{3+} show exceptional behaviour. In butanol-formic acid (1:9), these have R_f values (Sn = 0.50; Sb = 0.62) even though most metal ions either 'tail' from the 'point of application or have zero R_f values. This behaviour and other structural effects have been explained in terms of the polarity of the chromatographic system.

Antimony is one of the metals, separation and determination by paper chromatography of which are rather difficult. We had developed earlier an anisole-formic acid solvent system[1] for the successful separation of Sn^{2+} and Sb^{3+} by paper chromatography. Later, during a study of the separation of various valence states of mercury and antimony, it was noticed that formic acid showed an unusual behaviour with respect to antimony[2]. It was therefore decided to study systematically solvent systems containing formic acid for the paper chromatography of metal ions and to interpret the change in R_f values with change in the nature and composition of the solvent systems used and to develop successful methods for the separation of tin and antimony from numerous metal ions.

Lederer[3] described the use of water for separating antimony from common metal ions. This method, however, suffers from some limitations. The concentration of Sb should be rather high, *i.e.*,0.1 to 0.3 mg. per drop. Even then the separation is not complete and some ions (e g., Bi^{3+}) are coprecipitated with antimony. Since no other paper chromatographic method for the separation of tin and antimony from numerous metal ions has been reported, an effort has been made to develop such a method.

EXPERIMENTAL

Formic acid (E. Merck, Darmstadt) was used. All other chemicals used were either reagent grade chemicals or these were purified by usual means. Whatman No. 1 paper was used throughout.

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TABLE I

In methanol—formic acid systems.

Cations.	M_5.	M_4.	M_3.	M_2.	M_1.	Cations.	M_5.	M_4.	M_3.	M_2.	M_1.
Ag^{+}	0.00	0.00T	0.00 T	0.00T	0.00T	Co^{2+}	0.78	0.70	0.72	0.76	0.84
Hg^{2+}	0.55	0-0.40	0.70TD	0.66	0-0.64	Ni^{2+}	0.71	0.73	0.69	0.60	0.75
Hg_2^{2+}	0-0.30	0-0.68	0-0.50	0-0.60	0-0.64	Zn^{2+}	0.70	0.71	0.68	0.80	0.70
Pb^{2+}	0-0.40	0-0.40	0-0.42	0-0.50	0-0.52	Ca^{2+}	0,64	0.76	0.70	0.70	0.70
Cu^{2+}	0.71	0.74	0.75	0.71	0.69	Ba^{2+}	0.50	0.50	0.58	0.60	0.80
Cd^{2+}	0.60	0.58	0.65	0.40	0.67	Sr^{2+}	0.54	0.50	0.55	0.71	0.73
Bi^{3+}	0.63	0.68	0.62	0.57	0.35	Mg^{2+}	0.70	0.68	0.62	0.60	0.76
As^{3+}	0.60	0.58	0.53	0.40	0.35	Be^{2+}	0.75	0.85	0.88	0.80	0.85
Sn^{2+}	0.72	0.71	0.81	0.83	0.60	U^{4+}	0.73	0.72	0.78	0.60	0.74
Sb^{3+}	0.70	0.70	0.75	0.70	0.50	Tl^{+}	0.24	..	0.33	0.60	..
Al^{3+}	0.80	0.76	0.70	0.72	0.78	Th^{4+}	0-0.80	0-0.80	0-0.70	0-0.85	0-0.78
Fe^{3+}	0.83	0.80	0.76	0.80	0.72	Zr^{4+}	0-0.60	0-0.60	0-0.50	0-0.60	0-0.65
Cr^{3+}	0.70	0.66	0.55	0.42	0.78	Ce^{3+}	0-0.75	0.75	0.76	0.81	0.86
Mn^{2+}	0.71	0.66	0.64	0.52	0.71	V^{4+}	0.71	0.70	0.72	0.68	0.76
						La^{3+}	0-0.80	0-0.70	0.72	0.70	0.74

TABLE II

In n-*butanol—formic acid systems.*

Cations.	B_5.	B_4.	B_3.	B_2.	B_1.	Cations	B_5.	B_4.	B_3.	B_2.	B_1.
Ag^{2+}	0.00	0.00	0.00	0.00	0.00	Zn^{2+}	0.00	0.08	0.38	0.50	0.73
Hg^{2+}	0.00	0.00T	0.41	0.55	0.00T&0.60	Ni^{2+}	0.00	0.05	0.20	0.42	0.72
Hg_2^{2+}	0.00	0.10	0.0&0.41	0.0&0.60	0.0&0.60	Co^{2+}	0.00	0.05	0.30	0.50	0.70
Pb^{2+}	0.00	0.00	0.08	0.30	0.51	Ca^{2+}	0.00	0.05	0.28	0.48	0.72
Cu^{2+}	0.00T	0.05	0.20	0.32	0.50	Ba^{2+}	0.00	0.00	0.28	0.55	0.60
Cd^{2+}	0.00	0.10	0.22	0.35	0.60	Sr^{2+}	0.00	0.10	0.30	0.60	0.65
Bi^{3+}	0.00	0.10	0.20	0.30	0.30	Mg^{2+}	0.00	0.10	0.30	0.60	0.72
As^{3+}	0.08	0.20	0.18	0.15	0.45	La^{3+}	0.00	0.00	0.00T	0.40	0.70E
Sn^{2+}	0.50	0.55	0.50	0.48	0.62	Ce^{3+}	0.00	0.00T	0.00T	0.52	0.70T
Sb^{3+}	0.62	0.60T	0.43	0.40	0.50	Zr^{4+}	0.00	0.00	0.00T	0.00T	0-0.8
Fe^{3+}	0.00	0.00T	0.40	0.50	0.75	Th^{4+}	0.00T	0.00T	0.00T	0-0.70	0-0.8
Al^{3+}	0.00T	0.00T	0.25	0.60	0.68	U^{4+}	0.00T	0.00	0.50	0.70	0.75
Cr^{3+}	0.00	0.00	0.31	0.60	0.68	V^{4+}	0.00	0.00	0.16	0.30	0.80
Mn^{2+}	0.00	0.10	0.30	0.40	0.70	Be^{2+}	0.00T	0.20E	0.32	0.66	0.80
						Tl^{+}	0.00	0.05	0.30	0.56	0.72

TABLE III

In allyl alcohol-formic acid systems.

Cations.	A_5.	A_4.	A_3.	A_2.	A_1.	Cations.	A_5.	A_4.	A_3.	A_2.	A_1.
Ag^{2+}	0.00T	0.00T	0-0.60T	0.00	0.00	Co^{2+}	0.00	0.25	0.42	0.50	0.80
Hg^{2+}	0.00T	0.71	0.0&0.50	0.60	0.70	Ni^{2+}	0.00	0.20	0.41	0.61	0.80
Hg_2^{2+}	0.00T	0.00	0.00	0.00	0.0 & 0.70	Zn^{2+}	0.00	0.20	0.40	0.50	0.80
Pb^{2+}	0.00	0-0.20	0-0.20	0-.60	0-0.70	Ca^{2+}	0.00	0.20	0.40	0.52	0.70
Cu^{2+}	0.00	0.24	0.42	0.45	0.69	Ba^{2+}	0.00	0.20	0.42	0.55	0.70
Cd^{2+}	0.00	0.36	0.40	0.67	0.68	Sr^{2+}	0.00	0.22	0.41	0.60	0.75
Bi^{3+}	0.00	0.35	0.40	0.50	0.53	Mg^{2+}	0.00	0.20	0.43	0.60	0.70
As^{3+}	0.46	0.41	0.42	0.40	0.40	Be^{2+}	0.00T	0.15	0.40	0.60	0.82
Sn^{2+}	0.65	0.67	0.57	0.55	0.52	U^{4+}	0.00	0.50	0.35	0.54	0.60
Sb^{3+}	0.65T	0.63 T	0.63	0.56	0.55	Tl^{+}	0.00	0.30	0.35	0.55	0.77
Al^{3+}	0.00T	0.41	0.57	0.50	0.80	Th^{4+}	0.00T	0.00T	0 0.30	0-0.60	0.78
Fe^{3+}	0.00	0.63E	0.60	0.65	0.80	Zr^{4+}	0.00	0-0.40	0-0.40T	0-0.50	00.80
Cr^{3+}	0.00	0.30	0.50	0.60	0.80	Ce^{4+}	0.00	0.25	0.32	0.50	0.80
Mn^{2+}	0.00	0.21	0.45	0.60	0.70	V^{4+}	0.00	0.16	0.20	0.44	0.66
						La^{3+}	0.00	0.30	0.50	0.60	0.81

TABLE IV

In cyclohexanol-formic acid systems.

Caations.	C_5.	C_4.	C_3.	C_2.	C_1.	Cations.	C_5.	C_4.	C_3.	C_2.	C_1.
Ag^{+}	0.00	0.00	0.00	0.00T	0.00	Zn^{2+}	0.00	0.10	0.20	0.57	0.68
Hg^{2+}	0.00T	0.00T	0.62T	0.60	0.71	Ni^{2+}	0.00	0.08	0.22	0.46	0.67
Hg_2^{2+}	0.00	0.00T	0.0 & 0.60	0.0 & 0.50	0.0 & 0.60	Co^{2+}	0.00	0.08	0.20	0.51	0.71
Pb^{2+}	0.00	0.18	0-0.20	0.38	0.00 & 0.50	Ca^{2+}	0.00	0.0	0.10	0.50	0.70
Cu^{2+}	0.00	0.10	0.10	0.40	0.52	Ba^{2+}	0.00	0.05	0.12	0.51	0.76
Cd^{2+}	0.02	0.10	0.25	0.45	0.70	Sr^{2+}	0.00	0.00	0.20	0.42	0.72
Bi^{3+}	0.00	0.20E	0.30	0.32	0.60	Mg^{2+}	0.00	0.00	0.10	0.50	0.75
As^{3+}	0.30	0.15	0.52	0.33	0.37	La^{3+}	0.00	0.06	0.15	0.62T	0.71
Sn^{2+}	0.57	0.61	0.65	0.60	0.57	Ce^{4+}	0.00T	0.08	0.13	0.51	0- 0.55
Sb^{3+}	0.63	0.66	0.62	0.63	0.62	Zr^{4+}	0.00	0.00	0.00T	0.60TD	0-0.70
Fe^{3+}	0.00	0.14E	0.30	0.62	0.73	Th^{4+}	0.00T	0.05	0.10	0-0.60	0-0.70
Al^{3+}	0.09	00.02	0.16	0.53	0.70	U^{4+}	0.00	0.18E	0.25	0.53	0.71
Cr^{3+}	0.00	0.00T	0.20	0.50	0.60	V^{4+}	0.00	0.00	0.10	0-0.40	0.60
Mn^{2+}	0.00	0.08	0.14	0.42	0.70	Be^{2+}	0.10	0.20T	0.22	0.52	0.80
						Tl^{+}	0.00	0.12	0.20	0.60	0.71

The paper chromatography was performed by the ascending technique; 3 × 15 cm strips were developed in gas jars. Time of conditioning and time of development were respectively 15 and 45 min.

The ions of the H_2S group were detected with yellow ammonium sulphide. Aluminon was used to detect Al^{3+}, Cr^{3+}, Fe^{3+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, Zn^{2+}, Mg^{2+}, and Be^{2+}. Alizarine was used as a spraying agent for La^{3+}, Ce^{3+}, Zr^{4+}, Th^{4+}, U^{4+}, and V^{4+}.

Solvent systems containing the following alcohols were studied: methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl, isoamyl, *t*-amyl, allyl, octyl, benzyl, and cyclohexyl. The results are summarised in Tables I-IV. The tables for the remaining nine alcohols have been omited for the sake of brevity. In the tables the following of abbreviations have been used: M for methanol, B for butanol, A for allyl alcohol, C for cyclohexanol. The alcohol-formic acid ratios used were: (1) 1:9, (2) 3:7, (3) 5:5, (4) 7:3, (5) 9:1.

The ratio numbers are shown in parentheses. The solvent number consists of a symbol to represent the alcohol used with a subscript to denote the ratio number. Thus M_1 stands for methanol-formic acid mixture in ratio number (1), *i.e.*, 1:9; M_2 signifies methanol-formic acid mixture in ratio number (2), *i.e.*, 3:7 and so on. R_f values of 29 common ions in 65 solvent systems are reported.

DISCUSSION

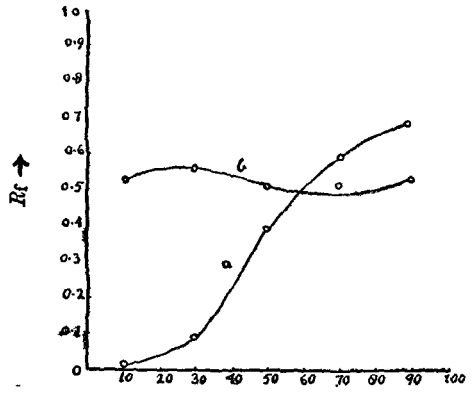
In most cases the plot of the R_f value of a metal ion against the percentage of formic acid in the system provides S-shaped curves (curve a, Fig.1). Very few attempts have been made to study and analyse this behaviour and to correlate the R_f value of a metal ion with changes in the nature and composition of the solvent system. It is true "that polarity, as some workers use it in reference to multi-component systems is some thing of a puzzle[4]". However, if we use two component systems of varying composition, keeping one of the components as fixed, the polarity of the system changes in a systematic manner and the chromotographic results under these conditions show a systematic pattern. Thus if the same acid is mixed with different alcohols, it should be possible to correlate the R_f value of a metal ion with the proportion and the nature of alcohol concerned.

Cassidy[5] reported that the R_f value of a particular amino-acid followed the order: methanol > ethanol > *n*-propanol = isopropanol > *t*-butanol, which is also the order of dielectric constants of the solvents. We have also found that for systems containing the same percentage of formic acid, the R_f values of most metal ions follow a similar pattern. At low acid concentrations, the R_f values are small because the system is only slightly acidic and because the equilibira involving ionic species are controlled by the acidity of the mobile phase. Low acidity favours the retention of the charged species by the aqueous gel. Taking *n*-butanol-formic acid system as an example, we find that in 9:1 ratio most metal ions either tail or have R_f values close to zero. This is because the small quantity of acid is not

4. Heftmann, "Chromatography", p. 102, Reinhold Publishing Co., 1961.
5. "Fundamentals of Chromatography", Interscience, New York, 1957.

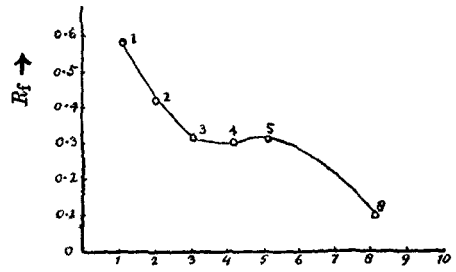
sufficient to check hydrolysis and to form the appropriate ions for migration. Of the 29 metal ions chromatographed, only Sn^{2+} and Sb^{3+} show an exceptional behaviour and have R_f values greater than 0.50. All the cations either tail from the point of appliction or have R_f values close to zero. This behaviour of Sn^{2+} and Sb^{3+} is probably due to the fact that these form uncharged complexes with formic acid, which have high partition coefficients in non-polar solvents. This unique behaviour of the two cations is further reflected in the fact that as the percentage of formic acid is increased, the R_f values of the two cations remain relatively stationary in all the systems studied (curve b, Fig. 1).

The behaviour of Ag^{+} and Hg_2^{2+} also needs some explanation. Ag^{+} does not migrate owing to possible reduction. Hg_2^{2+} probably disproportionates. This may be deduced from the fact that frequently Hg_2^{2+} gives rise to double spot formation. One spot has zero R_f value for metallic mercury and the other spot has an R_f value close to that Hg^{2+}.



% *Formic acid.*

FIG. 1. R_f values in formic acid—alcohol system.
(a) Most metal ions.
(b) Sb^{3+} and Sn^{2+}.



No. of C *atoms.*

FIG. 2. Change in R_f of most metal ions with increase of C atoms in alcohols.
1-8 refer respectively to MeOH, EtOH, *n*-PrOH, *n*-BuOH, *n*-AmOH, and *n*-octyl alcohol.

At low formic acid concentration, e.g. (0-20%), the increase in R_f value with increase in formic acid concentrations is slight due to non-availability of sufficient formic acid to check hydrolysis and to form appropriate ionic species. At high formic acid concentrations (70%), the increase in acid concentration does not significantly change either polarity of the system or the ionic species present. Hence the R_f values do not show a marked change. It is only in the range of 20-70% formic acid concentration that the R_f values of metal ions are most sensitive to the acid concentration and this is reflected in the increase in the slope of the curve. In this way we can qualitatively explain the form of an 'S'-shaped curve.

This general trend is noticeable in almost all systems whatever may be the alcohol used. Methanol is one exception. In this case the R_f values do not change significantly with change in formic acid concentration. The departure from the general behaviour may be attributed to the high D. E. C. of methanol (32.63). Addition of formic acid to methanol does not change significantly the polarity of the system and the R_f values remain almost unaltered.

From the plot of the R_f values against the number of carbon atoms present in various saturated straight-chain alcohols, it is noticed that once again an S-shaped curve is obtained (Fig. 2). In this case, the lower alcohol is more polar and therefore gives rise to a higher

R_f value for the cations. An increase in the number of carbon atoms decreases the polarity of the systems and hence the R_f values also keep on decreasing. When *n*-propanol is replaced by an unsaturated alcohol, like allyl, there is in general an increase in the R_f values owing to the higher dielectric constant of the system. For similar reasons it has been noticed that R_f values are in most cases higher in branched chain alcohols when compared with their straight-chain isomers. Similarly R_f values in benzyl alcohol and in cyclohexanol systems can be explained on the basis of the polarity of the systems. There are a few exceptions to this general trend, which need further study before definite conclusions can be reached.

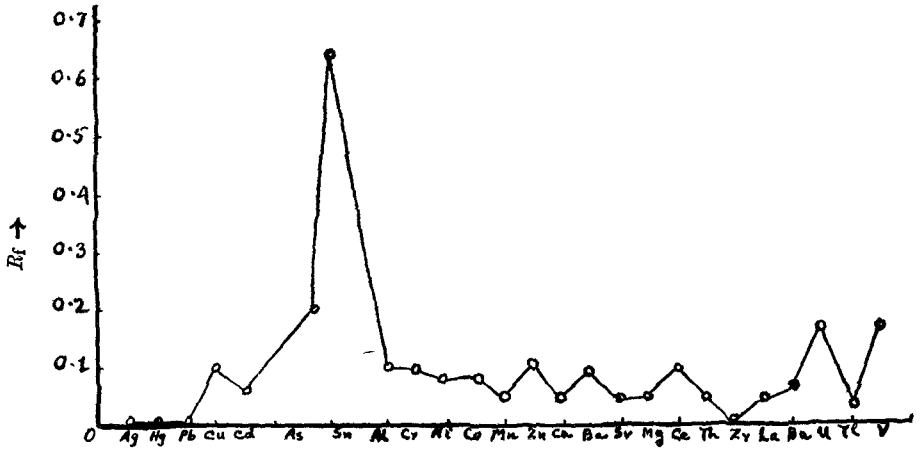


FIG. 3. Separation of Sn^{2+} with cyclohexanol-formic acid (7:3).

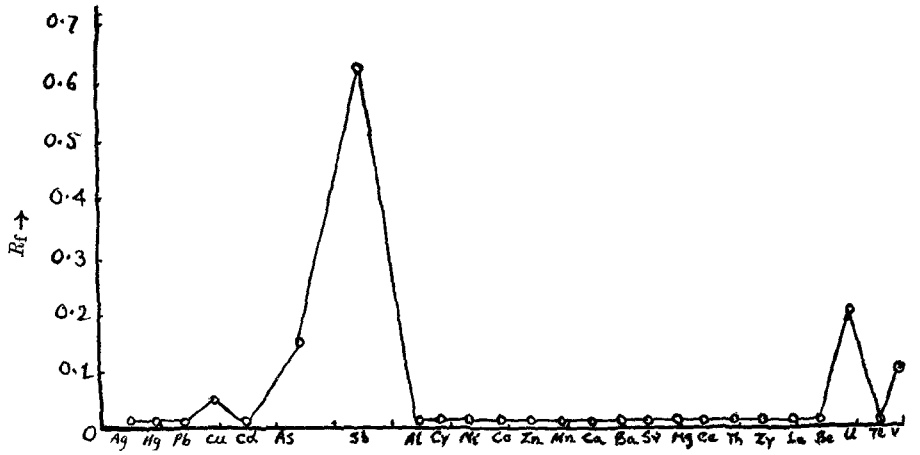


FIG. 4. Separation of Sb^{3+} with cyclohexanol-formic acid system (7:3).

Formic acid-cyclohexanol (3:7) system proved very efficient for the separation of Sn^{2+} and Sb^{3+} from numerous metal ions (Fig. 3 & 4). Separation of binary mixtures containing a particular cation and Sn^{2+} or Sb^{3+} was tried. In each case successful separation was obtained; only Hg^{2+} and Fe^{3+} interfered. Sn^{2+} and Sb^{3+} have R_f values close to 0.65, whereas

other metal ions have R_f values equal to or lower than 0.20. This solvent can therefore be used with advantage for the isolation of tin and antimony from numerous metal ions.

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Fast Paper Chromatography of Different Valence States of Mercury and Antimony

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Fast Paper Chromatography of Different Valence States of Mercury and Antimony

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▶ **A decrease in the separation time of metals in differing valence states is effected by use of a suitable solvent system. A number of solvent systems are studied for the separation of Hg_2^{+2}–Hg^{+2} and Sb^{+3}–Sb^{+5}. The most selective separation of Hg_2^{+2}–Hg^{+2} is obtained with a mixture of HNO_3–HCl–isopropanol; Sb^{+3}–Sb^{+5} separations are efficient in a mixture of acetic acid–water–ethyl acetate. R_f values are given for ions which are likely to interfere in the procedure, and the phenomenon of double spots is discussed.**

THE TIME of separation is a particularly important factor in the paper chromatographic separation of a metal in different valence states. If the separation time is long enough, some interconversion of valence state may occur. Also, one of the valence states—Sb^{+5} in the present case—may be sufficiently reactive to interact slowly with the paper or the solvent system. Several techniques may be utilized to decrease the separation time, including the use of a higher temperature, centrifugal chromatography, or choice of a proper solvent system. A higher temperature may increase the rate of interconversion, as well as decrease the separation time, and centrifugal chromatography requires specialized equipment. Therefore, the choice of a proper solvent system offers the simplest solution to the problem.

The importance of the study of such separations has been discussed previously (*1–3*). A fast solvent system (*3*) was reported for the separation of Fe^{+2} and Fe^{+3}. This paper summarizes recent findings on the separation of different valence states of Hg and Sb. These separations were reported earlier by Bighi (*1*) and Pollard (*2*). We could not reproduce Bighi's separation of Hg_2^{+2} and Hg^{+2}. The separation of Sb^{+3} and Sb^{+5}, as reported by Pollard, requires 1 hour, and Sb^{+5} tails. Neither Bighi nor Pollard mentions the selectivity of the separations. Therefore, we have made a more detailed study and developed faster and more selective solvent systems.

EXPERIMENTAL

Apparatus. Development was performed in 20-X 5-cm. glass jars, using the ascending method. The dimensions of the paper strips were 15 × 4 cm.

Reagents. All results were obtained on Whatman No. 1 paper using reagent grade chemicals. All solvents were purified by distillation.

Mercury Test Solution. Three grams of freshly prepared mercurous nitrate (mercurous nitrate E. Merck, which contains an appreciable quantity of mercuric nitrate, was treated with dilute nitric acid and mercury until colorless crystals of mercurous nitrate appeared) were dissolved in 50 ml. of approximately 3*M* HNO_3. Two grams of mercuric nitrate were boiled with 5 ml. of concd. HNO_3. Spotting was done with 0.1*M* solutions. Ammonia gas and ammonium sulfide were used as detectors.

Antimony Test Solution. The Sb^{+3} solution, 0.2*M*, was prepared as reported earlier (*4*). The 0.2*M* $SbCl_3$ solution in HCl was boiled with $KClO_3$, cooled, and filtered. This was used as the Sb^{+5} solution. Ammonium sulfide and H_2S gas were used as detectors. Rhodamine B was used for the detection of Sb^{+5} only.

RESULTS

To develop suitable methods of separation, a number of pure solvents were examined. The results are summarized in Table I.

Separation of Hg_2^{+2} and Hg^{+2}. The following solvent systems gave fast separations of Hg_2^{+2} and Hg^{+2}: 0.1*M* HCl (S_1); 15% aqueous am-

monium acetate–3M HNO_3–3M HCl (6:1:1) v./v. (S_2); 3M HNO_3–3M HCl–isobutanol (1:1:10) v./v. (S_3); and 3M HNO_3–3M HCl–isopropanol (1:1:10) v./v. (S_4). In all these solvent systems, Hg_2^{+2} has an R_f value of 0.00.

S_1 is the simplest system giving fast separations (R_f Hg^{+2} = 0.81). When the concentration of HCl is gradually varied from 0.1M to approximately 3.00M, the two R_f values as expected remain almost constant. In 3M HCl, the Hg_2^{+2} spot is rather elongated. In S_2, Hg^{+2} has an R_f value of 0.84. When the proportions of Hg^{+2} and Hg_2^{+2} in the sample were gradually varied from 4:1 to 4:16, the two R_f values remained constant. When the concentration of the sample applied was *gradually altered from 0.2 to 0.01M, no* significant change either in efficiency of separation or in the R_f values was found. After 5 minutes of development the distance between the spot boundaries was 1.9 cm. Of the common cations studied as impurities, only Ag^+, Sn^{+2}, and Bi^{+3} affected the separation. In all other cases, good separations were obtained. Sn^{+2} affects the separation by its reducing action on the Hg_2^{+2}–Hg^{+2} system. In S_3, Cd^{+2} (R_f = 0.30), Bi^{+3} (R_f = 0.30), and As^{+3} (0.40) have R_f values significantly different from those of Hg_2^{+2} and Hg^{+2} (R_f = 0.61). S_4 is even more selective than S_3. Cations having R_f values different from those of Hg_2^{+2} and Hg^{+2} (R_f = 0.66) are As^{+3} (0.43), Sn^{+2} (0.90), Fe^{+3} (0.30), Al^{+3} (0.20), Cr^{+3} (0.30), Mn^{+2} (0.22), Ca^{+2} (0.20), Ba^{+2} (0.20), Sr^{+2} (0.24), and Mg^{+2} (0.22). Cations with R_f values not significantly different from Hg^{+2} are Cd^{+2} (0.63), Bi^{+3} (0.60), and Sb^{+3} (0.61). Cations with R_f values not significantly different from Hg_2^{+2} include Ag^+ (0.00) and Pb^{+2} (0.00 T).

Double Spot Formation. Hg_2^{+2} gives two spots when developed with 15% ammonium acetate solution and 20% ammonium chloride solution. In both cases the R_f values are 0.00 and 0.84. Since mercurous is not known to form any complex, the possibility is that one spot is due to mercurous nitrate while the other spot is due to mercurous acetate (when developed with ammonium acetate) and mercurous chloride (when developed with ammonium chloride). However, when hydrochloric acid is added to ammonium acetate, the double spot formation is prevented because in this case mercurous nitrate is efficiently converted to mercurous chloride.

Separation of Sb^{+3} and Sb^{+5}. A number of developers were tried for this separation—e.g., isopropyl ether, chloroacetic acid, benzyl cyanide, dioxane, ethyl acetate, ethyl propionate, acetic acid, propionic acid, butyric acid, acetone, pyridine, acetyl acetone, cyclohexanone, acetophenone, ethyl methyl ketone, propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, tertiary butyl alcohol, and anisole. None of these were successful. Separations were obtained, however, by using glacial acetic acid–water–ethyl acetate (1:1:1). This solvent will be called S_5.

Mixtures containing Sb^{+3} and Sb^{+5} in ratios varying from 1:3 to 9:3 were efficiently separated by this method. The R_f of Sb^{+3} fluctuated from 0.65 to 0.71, while Sb^{+5} was always at the solvent front. Almost all important cations were developed with S_5. The cations whose R_f values differ significantly from those of Sb^{+3} and Sb^{+5} are given in Table II.

Of the common cations tried, the following have R_f values close to that of Sb^{+3}. R_f values: Hg^{+2}, 0.76; Cu^{+2}, 0.75; Sn^{+2}, 0.78; Al^{+3}, 0.64; Cr^{+3}, 0.60; and Mn^{+2}, 0.60. None of the cations tried have R_f values close to Sb^{+5}.

Double Spot Formation. Sb^{+3} gave double spots in a number of cases which are shown in Table III.

Table I. R_f Values in Various Solvents

S No.	Solvent	R_f values Sb^{+3}	Sb^{+5}	Hg^{+2}	Hg_2^{+2}
1	Formic acid	0.50	0.40	0.80	0.00 & 0.80
2	Acetic acid	0.21–0.53	0.70	0.50	0.00 T.
3	Propionic acid	0.30	0.48	0.00, 0.60	0.00 T.
4	Butyric acid	0.00 T.	0.20	0.00, 0.20	0.00 T.
5	Ethyl acetate	0.00, 0.12	0.00 T. to S.F.	0.00	0.00 T.
6	Propyl acetate	0.00, 0.20	0.00 T. to S.F.	0.00	0.00
7	Methyl alcohol	0.00 T.	0.71	0.00 T.	0.00 T.
8	Isoamyl alcohol	0.00	0.00, 0.90	0.00 T.	0.00 T.
9	Allyl alcohol	0.64	T. down from S.F.	0.64 T. down	0.00
10	Dioxane	0.00 T.	0.3–0.61	0.00 T.	0.00 T.
11	Isopropyl ether	0.00	0.15	0.00	0.00
12	Anisole	0.02	0.05	0.00	0.00
13	Acetone	0.00, 0.20	0.93	0.00 T. to S.F.	0.00
14	Ethyl methyl ketone	0.00, 0.15	1.00	0.00	0.00
15	Acetyl acetone	0.00, 0.20	0.00 T. to S.F.	0.00	0.00
16	Isopropyl alcohol	0.72	0.80	0.00	0.00 T. to S.F.
17	Water	0.00 T.	0.64	0.00, 0.61	0.00 T.

Abbreviations: S. F. = solvent front; T. = tails.

Table II. Noninterfering Cations

Cation	R_f	Cation	R_f
Ag^+	0.00(tails)	Co^{+2}	0.47
Pb^{+2}	0.40	Ni^{+2}	0.33
Ca^{+2}	0.58	Zn^{+2}	0.54
As^{+3}	0.50	Sr^{+2}	0.55
Fe^{+3}	0.53	Mg^{+2}	0.50

Table III. R_f Values of Double Spots of Sb^{+3}

Developer	R_f Values First spot	Second spot
Ethyl acetoacetate	0.00	0.14
Benzyl cyanide	0.00	0.12
5% Solution of thiourea in butanol	0.00	0.50
12M Chloroacetic + isopropyl ether (1:1)	0.00	0.20

DISCUSSION

The separation of Hg_2^{+2} and Hg^{+2} proved more difficult than expected. Acetic acid differentiates fairly well between Hg_2^{+2} and Hg^{+2} (Table I). A number of solvent systems containing nitric acid, acetic acid, and water in different ratios were tried. In most of these solvents, Hg_2^{+2} and Hg^{+2} when separate gave different R_f values, but when a mixture of the two cations was used the separation was not distinct. Best results were obtained with S_6—i.e., acetic acid–3M HNO_3–water (3:1:2). If the concentration of nitric acid was less than that in S_6 the mercurous ion was not completely transferred from the point of application, owing to its strong interaction with paper. If, on the other hand, the concentration of nitric acid were increased, the Hg_2^{+2} was transferred completely from the point of application. The solvent system was then so polar, however, that the paper did not function as differentiating medium between the two cations. To achieve fast and efficient separations, precipitation chromatography was tried using S_1 and S_2. These solvents proved to be fast but nonselective. Pb^{+2} and Ag^+ had R_f values close to zero, while all the other common cations had R_f values close to those of Hg^{+2}.

To attain both speed and selectivity, complexation chromatography was superimposed on precipitation chromatography. Methyl alcohol was

added to the HCl–HNO_3 system. The result was that mercurous ion began to tail, owing to its strong interaction with methyl alcohol. When methyl alcohol was replaced by isobutyl alcohol, the system became less polar and Hg_2^{+2} gave a compact spot. Three ions gave R_f values significantly different from those of Hg_2^{+2} and Hg^{+2}. With isopropyl alcohol, which is intermediate in polarity between methyl alcohol and isobutyl alcohol, the system became fast, selective, and efficient.

A reference to Table I shows that Sb^{+3} and Sb^{+5} have different R_f values in a number of organic solvents—i.e., acetic, propionic, and butyric acids; dioxane, acetone, ethyl methyl ketone, methyl alcohol, and isopropyl ether. And, therefore, a number of excellent separations are possible with slight modifications in these solvents. All efforts to separate Sb^{+3} and Sb^{+5} using individual organic solvents failed because most of them were not sufficiently polar. Acetic acid gave an elongated spot owing to its low ionization. The addition of water increased the ionization of acetic acid sufficiently to give compact spots. Because of the high polarity of the system, however, ΔR_f was very small. The addition of ethyl acetate decreased the polarity of the system to such an extent that ΔR_f became significant.

It was noticed in this study that the higher valence state almost always had the higher R_f value. This is easily understood because the higher valence state has a greater covalent character and therefore a greater complexing power. Of the solvents we studied only formic acid appears to be an exception to this trend. The R_f of Sb^{+5} in formic acid is smaller than that of Sb^{+3}.

In the homologous series of fatty acids studied, the R_f values decreased with an increase in molecular weight owing to a decrease in the polarity of the system. In this case also formic acid is an exception. The R_f value of Sb^{+5} in formic acid is less than in acetic acid. We are making a more complete study of the behavior of formic acid and the findings will be reported later.

The importance of time of separation in such cases has been emphasized earlier. To incorporate it in paper chromatography we suggest that the time required for a 1-cm. separation between spot boundaries should be mentioned where necessary along with other data. A paper chromatographic separation may be classified as fast, rapid, normal, slow, or extra slow according as this time (t) is 0 to 30 minutes, 30 minutes to 1 hour, 1 to 6 hours, 6 to 24 hours, or more than 24 hours, respectively. Time for the Hg_2^{+2}–Hg^{+2} separation with S_3 and S_4 is 10 minutes, and for the Sb^{+3}–Sb^{+5} separation with S_5 is 20 minutes. Hence, both these separations may be classified as fast.

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